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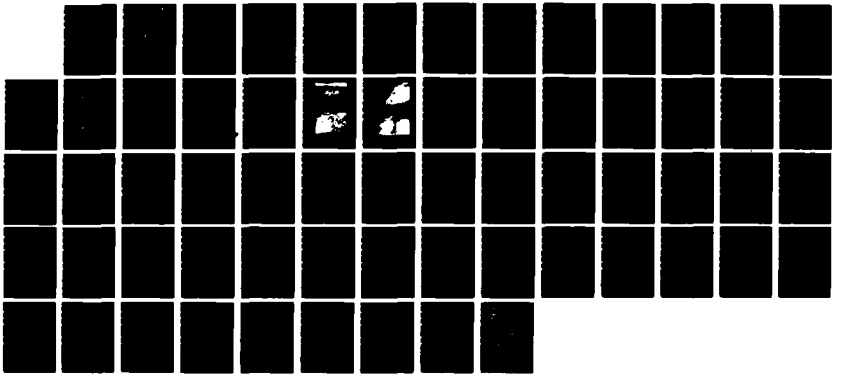

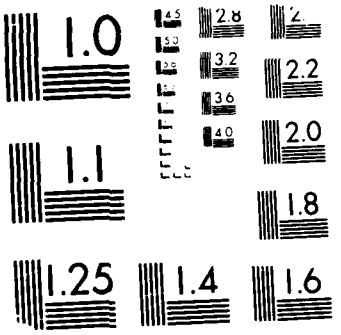

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CHEMICAL RESEARCH, DEVELOPMENT & ENGINEERING CENTER

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CHEMICAL CHARACTERIZATION OF HC SMOKE POT RESIDUE

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U.S. ARMY ARMAMENT MUNITIONS CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

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The objective of this research was the chemical characterization of residues from hexachloroethane (HC) smoke pots generated using several ignition scenarios under field conditions. Two trials were conducted: the first examined the spatial distribution of organic and inorganic compounds in the smoke pot residue, and the second examined the effects of burn scenario (number of smoke pots and pot orientation) on the compositions of smoke pot and deposited residues. In the first trial, core samples were taken near the edges of the smoke pot and in the center. The samples were divided into subsections representing the bottom, middle, and top. Chemical analysis showed that the residue, representing 17-23% of the original mass, was primarily Al_2O_3, C, $ZnCl_2$, $FeCl_3$, and FE_2O_3, across sections but not depths, whereas cadmium concentrations differed by section and depth. In the second trial, single or double smoke pots were ignited upright or on their sides. Smoke pot residue compositions were little affected by either the number of smoke
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pots or their orientation, although these did affect the quantity and composition of deposited material. The mass deposited by an upright pot was 6-8 times the mass deposited by a pot on its side. However, the concentrations of inorganics and organics were higher in residues deposited from horizontally-fired smoke pots.

PREFACE

The work described in this report was authorized under Military Interdepartmental Purchase Request (MIPR) 5311 1437. This work was started in March 1985 and completed in August 1986.

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This report has been approved for release to the public.

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CHEMICAL CHARACTERIZATION OF HC SMOKE POT RESIDUE

INTRODUCTION

Background

Obscurant smokes are used by the Army during training. One of these is hexachloroethane smoke (HC-smoke), which is produced by reaction of hexachloroethane (46.7%), zinc oxide (46.7%) and granular aluminum (6.7%). The hexachloroethane and zinc oxide ratio is generally maintained close to 1:1 while the aluminum content is varied slightly to regulate the burning rate (USA 1975). Equation 1 gives the chemical reaction in smoke formation.

$$C_2Cl_6 + 3ZnO + 2Al \text{ -------} > 3ZnCl_2 + Al_2O_3 + 2C + \text{heat} \quad \text{(Eq. 1)}$$

The $ZnCl_2$ vapors, after rapid condensation, form the desired obscurant particulates. The vapor and particulate matter emitted by the HC smoke mixture have been chemically characterized in test burns with simulated "mini" smokepots by Katz et al. (1980). Major constituents have been monitored in field tests and their relative concentrations determined at various distances from the source (Schaeffer et al. 1986, 1987).

A health risk assessment of HC smoke found that the carcinogenic potential of the chemical by-products formed during the smoke generation process created a high excess risk to military personnel (Novak et al. 1983). The study did not consider the possible effects of residues on environmental and human health. Although the vapors and particulate matter emitted from HC smokepots have been chemically characterized, the chemical compositions of smokepot and deposited residues are unknown. As shown in this study, pot and deposited residues are each about 20 % (2000 g) of the smokepot charge (13,600 g).

The effects (if any) of residues on human health and the environment are not known. Information on the chemical composition of the residues is needed to determine the hazards associated with spent smokepots. The Army does not have a published standard operating procedure for collecting and disposing of used smokepots in an environmentally acceptable manner. Before alternative acceptable disposal measures can be employed, the smokepot residues must be chemically characterized. Based on this characterization, alternative Preventative Environmental Technology (PET) measures can be developed and tested.

Objective

A three phase study of HC smokepot residues is planned. This research will determine the need for preventative measures to avoid environmental contamination and for development of safe disposal methods for workers. Phase I, reported here, character-

ized the chemical composition of HC smokepots and deposited residues generated using a fixed set of field experimental conditions. Experimental procedures for chemical characterization of residues were evaluated and documented. Extensive recommendations for additional studies and for suggested actions are made.

Approach

A literature review was conducted to determine the most probable chemical compounds or predominant chemical groups characterizing HC smokepot residues. Based on this literature review, an analytical scheme to identify and quantify smokepot residue chemical constituents was developed and validated. The scheme was a comprehensive mass balance accounting procedure which attempted to identify compounds which might adversely effect the localized environment. A statistical design for sampling smokepot and deposited residues was developed. This plan treated the smokepot residues as a segmented "lot' sampling problem (defined in Appendix A).

Samples were collected at 9 levels within the smokepot. At least 5 points outside the smokepot on the downwind axis, and at least 3 points outside the smokepot on the other axes, samples were collected in a manner which generated sufficient data to examine deposition quantity versus distance relationships. An experimental procedure to systematically collect smokepot residues under field conditions was developed.

The study was conducted in two trials. Trial 1 was designed to develop and evaluate experimental protocols for generating HC-smoke, collecting residues in the field, and chemical analysis. Laboratory experiments optimized the recovery of likely inorganic and organic compounds. A comprehensive analytical scheme designed to identify all major, and many minor chemical compounds in the residues was developed for Trial 2. Analyses were optimized using model inorganic and organic species which had been selected based on the literature review. The analytical scheme was based on one used to identify complex organic compounds in coal gasification products (Vogt et al. 1982). The scheme was validated for smokepots using HC residues and contaminated sands obtained in an earlier study. Strict attention was given to QA/QC procedures to assure the validity of analytical results.

Scope

Phase I was concerned with the development of field sampling and chemical analysis methods. The reproducibility of smokepot burn times was investigated. A primary concern was the lateral and vertical distributions of compounds in the smokepot residue. Another primary concern was determining how the burn scenario

affected the spatial distribution and chemical composition of deposited residues. Scenarios using single and double smokepots ignited upright or on their side(s) were studied. Phase I was not concerned with the effects of air temperature, humidity, age of the smoke munition, or differences in munitions from different Lot numbers. It was not possible to measure the temperature in the ignited smokepot. The ecological and human health risks associated with smokepot and deposited residues were not investigated. This study was not concerned with the environmental fate of deposited residues or with disposal methods for spent smokepots and contaminated soils.

Mode of Technology Transfer

USA-CERL technology transfer will occur through preparation of a USA-CERL Interim Technical Report, in Process Reviews, presentation at appropriate DOA conferences, and publication in the technical literature. USA-CRDEC, sponsor of this work, will be responsible for the ultimate technology transfer, including publication of a technical report.

The findings and recommendations will lead to further research in HC smokepot chemistry, biomonitoring, environmental impact and risk assessment. These include (1) studies of the deposition of HC residues, (2) effects of humidity on residue chemistry and distribution, (3) environmental fate of deposited chemicals, (4) development of disposal procedures for spent smokepots and procedures for cleanup of contaminated soils (defined by USA-CRDEC as Preventive Environmental Technology). The results reported here may effect new guidance for the safe disposal of use of HC smoke and smokepot residues.

PROCEDURE

Literature Review

The basic chemical processes in HC-smoke generation are understood (Eq. 1). However, the complex reactions occurring in an HC smokepot are largely unknown. The actual reactions are very complex as evidenced by the formation of by-products such as phosgene ($COCl_2$), trichloroacetyl chloride (CCl_3COCl), tetrachloroethylene (C_2Cl_4), hexachlorobenzene (C_6Cl_6) and carbon tetrachloride (CCl_4). Furthermore, while the effects of the mix composition, age, addition of dyes, and moisture content, on the stability, optical properties of the obscurant smoke, and rate of reaction, have been monitored (Hartley et al. 1982, 1984), little attention has been paid to the possible formation of chlorinated-oxygenated aromatics at the high temperatures obtained during HC-smoke generation. In order to delineate the possible reactions occurring at the high temperatures (>1100°C) reached during HC-smoke generation, literature related to the reactions of chlorinated hydrocarbons at high temperatures was reviewed. Special attention was given to processes where the chlorinated hydrocarbons react in the presence of a reducing environment promoting free radical reactions (Senkan 1982).

Studies reporting the formation of environmentally significant molecules such as polychlorinated oxygenated aromatics, chlorinated organometallics and chlorinated polynuclear aromatics was reviewed (Exner 1982, and references therein). Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated xanthanes, and others, have been found in simulated incineration studies at temperatures up to 650°C (Markund et al. 1985). Some of these compounds are toxic to several faunal species, so their presence in smokepot residue would increase the environmental risk associated with the use of HC obscurant smoke. However, the extent of survival of most organic molecules at the temperatures reached during the smoke generation process is largely unknown. Kinetic and thermodynamic data suggest that most compounds are destroyed at high temperature. However, because chlorinated hydrocarbons suppress combustion rates at elevated temperatures, i.e., temperatures above ~800°C (Senkan 1982) (due to their free radical scavenging characteristics), contact time in the heated zone may markedly affect the extent of destruction. Thus, present incineration guidelines suggest a 2.0 sec dwell at 100°C or a 1.5 sec dwell at 1600°C (Clark and Cudahy 1982).

Generation of Smoke and Collection of Residue Samples

Residues from HC smokepots were collected in two trials conducted at Fort Leonard Wood, Missouri. In Trial 1 (24-25 June 1985), five smokepots from Lot # PB-84 M024-007 were set off, one at a time, in upright positions. The purposes of this trial were to confirm the sampling and analytical methods and to determine the spatial distribution of components in the smokepot residue. The second trial (16-19 December 1985) examined the effect of commonly employed smokepot ignition modes on residue composition. In both trials, deposited residues were sampled using a grid shown schematically in Figures 1-2.

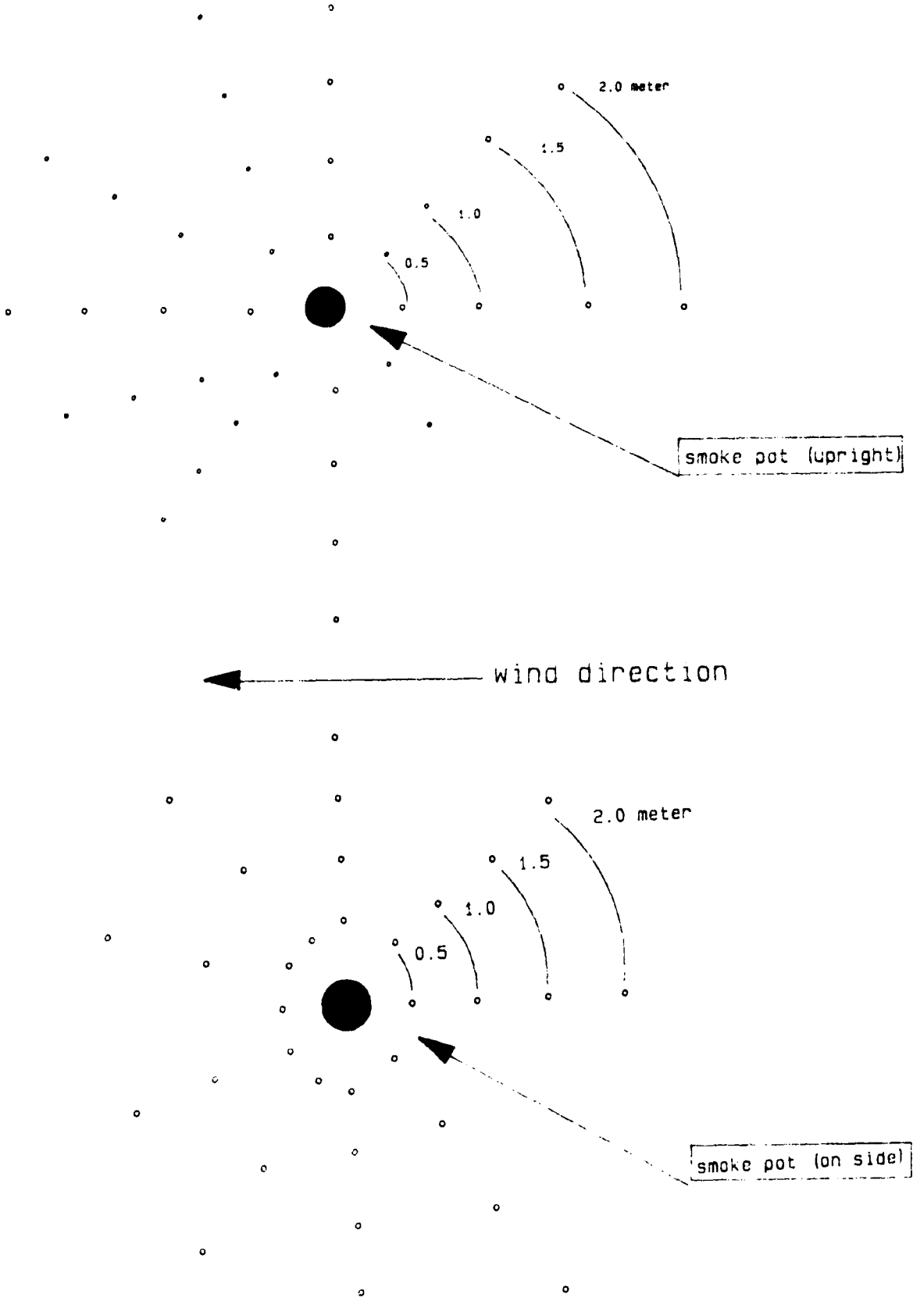


FIGURE 1: SCHEMATIC OF THE CONTAMINATED AREA SAMPLING GRID

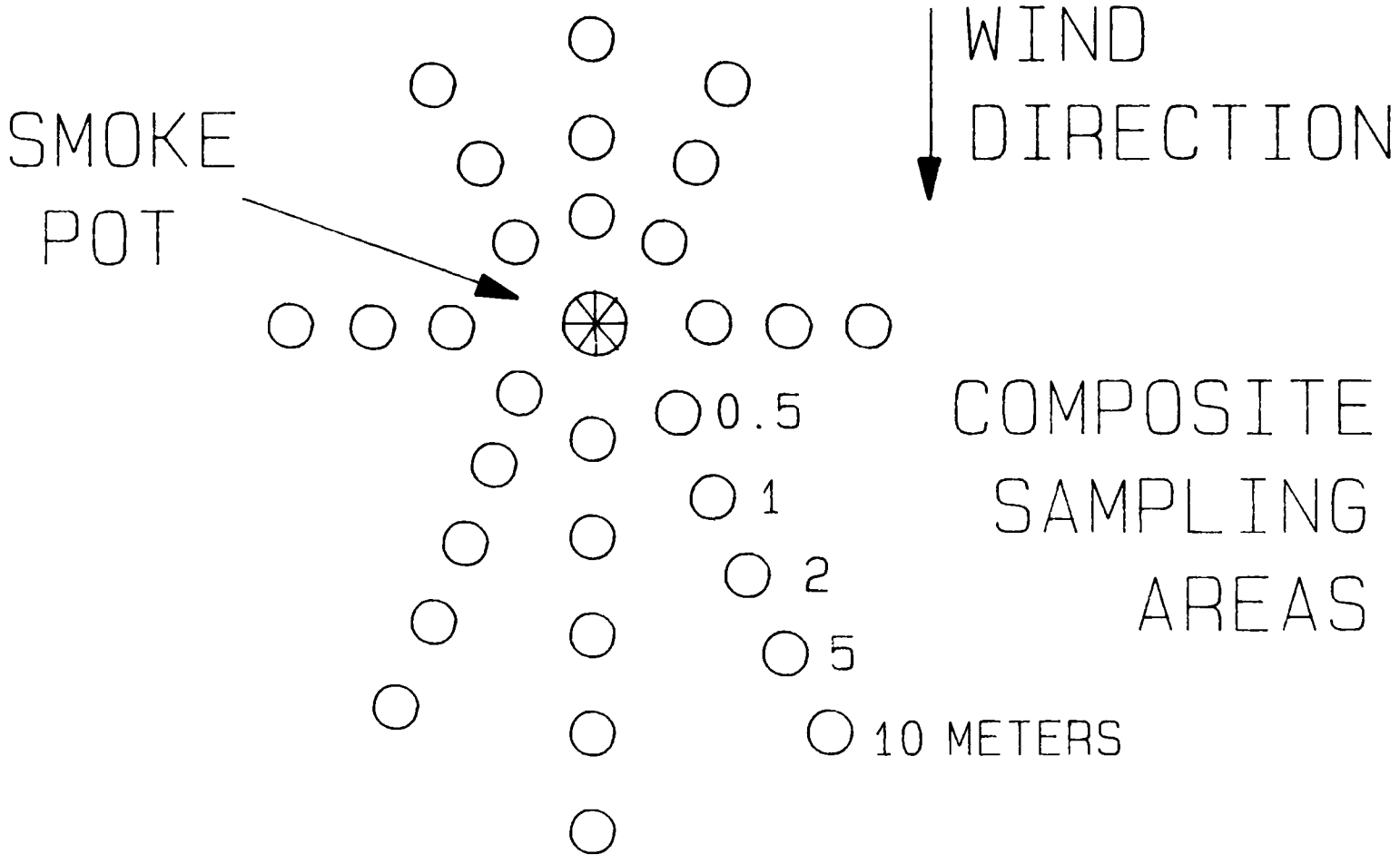


FIGURE 2: CONTAMINATED AREA SAMPLING

Expended smokepots from Trial 1 were subsampled to determine the spatial distribution of components in the residue. Smokepots were sampled by cutting the smokepot with shears. The smokepot residue was divided into three sections (A, B, C) with a stainless steel sampler designed for that purpose. Each section was divided into three subsections (1, 2, 3) (Figure 3). In addition to sampling the residues in the smokepots, deposited residues were collected by placing pyrex glass dishes 0.5 to 10 m from the smokepot. Burn rate, total residue content, humidity and air temperature were monitored.

Trial 2 studied four ignition modes: a single smokepot fired in upright position, two smokepots stacked and fired in upright position, a single smokepot fired on its side, and two smokepots placed back to back and fired on their sides. The placement of pots and sampling trays for each mode is shown in Figures 4-5. In order to make a statistically sound assessment of any changes in composition resulting from the ignition mode, each mode was repeated five to six times. A total of 34 HC-smokepots were used. Thirty smokepots were from Lot # PB-84 M024-007 ("Lot 1") and 4 from Lot # PB-84 C020-012 ("Lot 2") were sampled. Residues deposited within 2 m from the smokepot were sampled. All residues were weighed, homogenized, and analyzed for inorganic constituents and total carbon, and screened for major organic moieties such as tetrachloroethane, hexachloroethane, hexachlorobutadiene and hexachlorobenzene.

Analysis for Organic Constituents

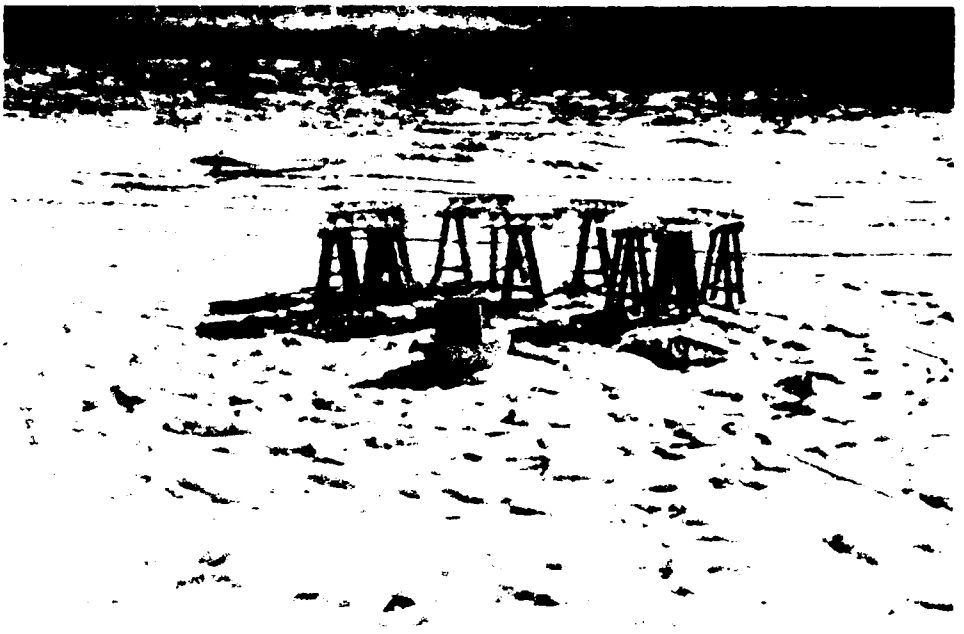
The analytical scheme was first optimized and validated with model compounds consisting of polynuclear aromatic hydrocarbons. polychlorinated aliphatics and aromatics. Residues from Trial 1 were spiked with known concentrations of model compounds. Recoveries were optimized by varying the extraction solvents. concentration techniques and fractionation procedures. Toluene and benzene were the most efficient solvents. Recoveries for D-labeled naphthalene, anthracene, chrysene, and dibenzanthracene were 90-100% with toluene and 75-90 % (Trial 1) and 85-100% (Trial 2) with benzene. Toluene was used in Trial 1. Because traces of $AlCl_3$ in the residue led to the formation of many condensation products with toluene, benzene was used in Trial 2.

The validated procedure (Figure 6) used in the analysis of residues from Trial 2 consisted of an 18 hr soxhlet extraction of 10-20 g residue with 300 ml glass distilled benzene (EM Science, Cherry Hills, NJ), concentration of the extract with rotary evaporation, and screening of the concentrated extract with high performance liquid chromatography (HPLC). The HPLC system used for initial screening was a model 4 solvent delivery system with a LC75 UV/VIS detector in tandem with a model 650-10S spectrofluorimeter (Perkin-Elmer Corp., Norwalk, CT). Separations were

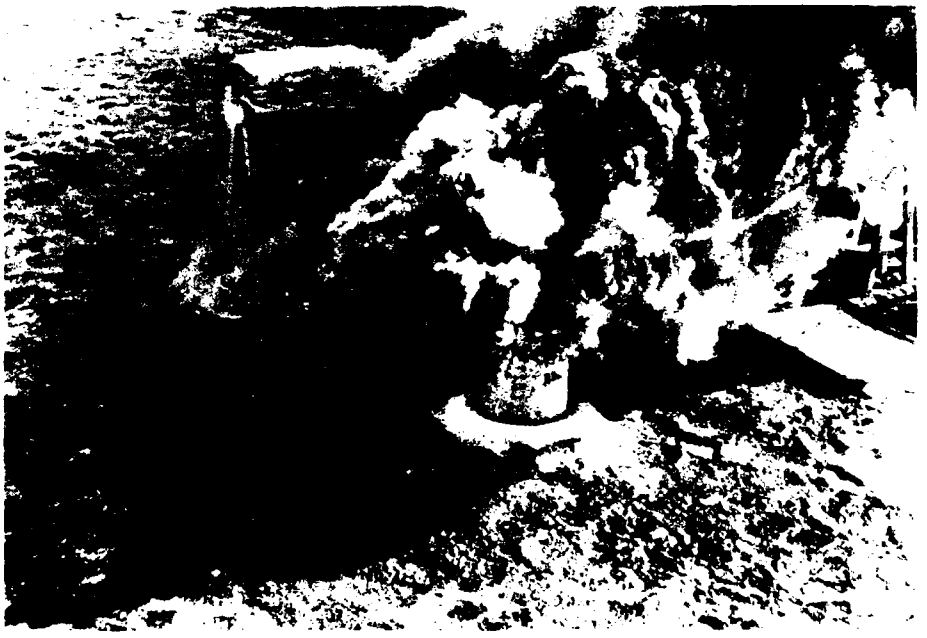
Figure 3

Subsampling Arrangement for Smokepots in Trial 1

C-1	B-1	A-1	B-1	C-1
C-2	B-2	A-2	B-2	C-2
C-3	B-3	A-3	B-3	C-3



(A)
Single: Upright



(D)
Double: Upright

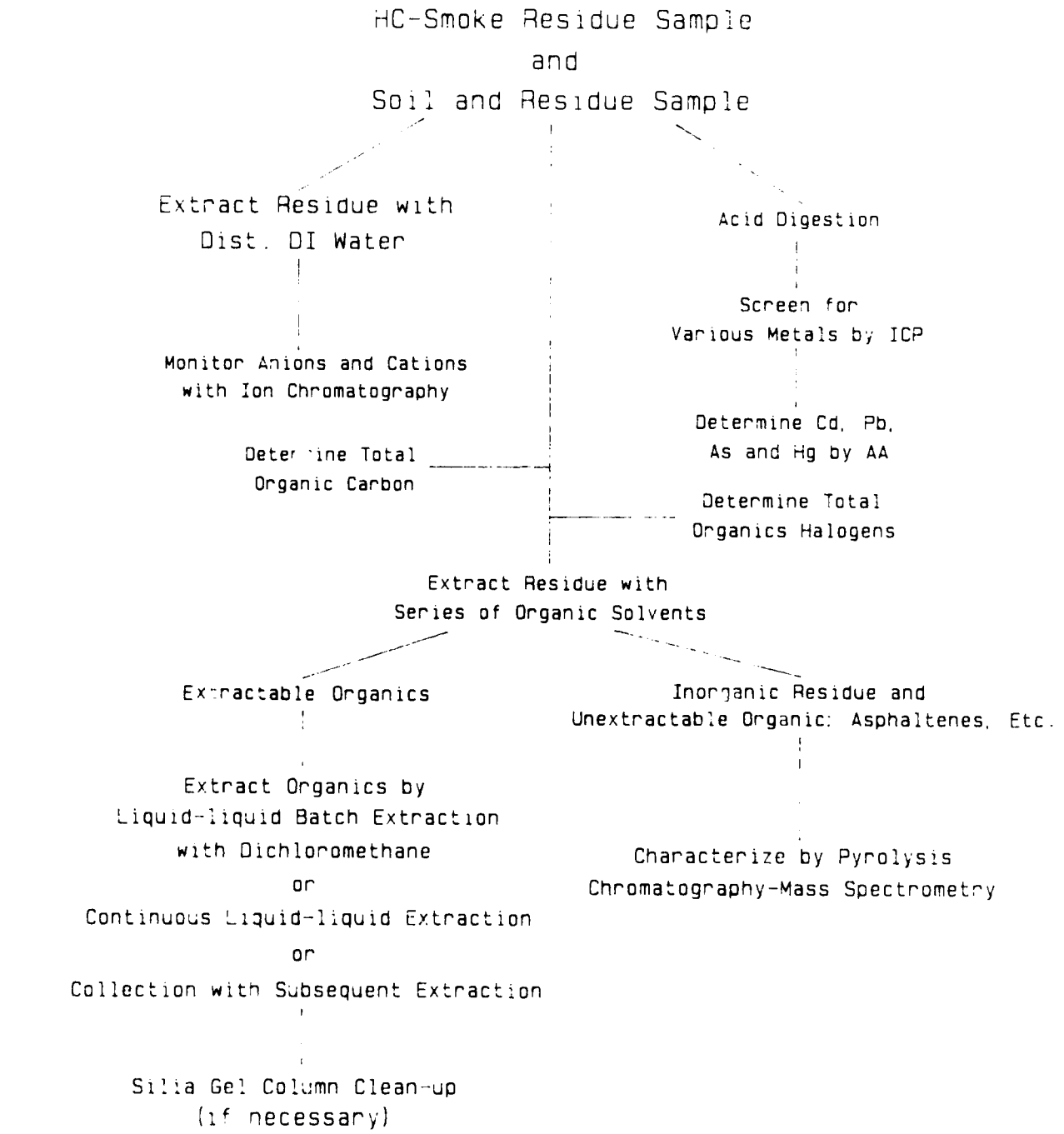
Figure 4. Photographs of burn modes used.

(C)
Single. On Side

(D)
Double: On Side

Figure 5. Photographs of burn modes used

Figure 6
Isolation, Fractionation and Characterization Scheme



carried out with a C-18 column under a four step solvent gradient. The eluent was (60/40) water:acetonitrile to 100 % acetonitrile. Absorption, excitation, and emission wavelengths were monitored as a function of time to optimize the sensitivity for ring polynuclear aromatics.

Residue extracts were analyzed for polyhalogenated aromatics and aliphatics using a gas chromatograph equipped with an electron capture detector (Model 560, Tracor Instruments, Austin, TX). Separation was carried out with a 30 m bonded phase fused silica capillary column (DB-5, J & W Scientific, Rancho Cordova, CA). Confirmatory analysis for extracted organic constituents used a gas chromatograph interfaced to a mass spectrometer (GC-MS) (Model OWA 30B, Finnigan Corp., Palo Alto, CA) operating at 55 eV. GC-MS analyses used a 30 m bonded phase fused silica capillary column. To assure the uniformity of the extraction procedure, all residue samples were spiked with known amounts of deuterium labeled naphthalene ($C_{10}D_8$), anthracene ($C_{14}D_{10}$) and chrysene ($C_{18}D_{12}$). Recovery was monitored by determining the areas of ions m/e 136, 188 and 240. The instrument was tuned and calibrated daily to meet US EPA decafluorotriphenyl phosphine (DFTPP) specifications (USEPA 1980).

Analysis for Inorganic Constituents

Residues were screened for 32 elements using inductively coupled plasma emission spectrophotometery (ICPES) (Model 975 Plasma Atom comp, Jarrell Ash, Waltham, MA). Because of the very high content of Al_2O_3 in the samples, solution was effected by fusion with lithium metaborate ($LiBO_2$). The fusion was carried out at 1050^{o}C after adding 0.25 g of homogenized sample to 0.8 g of $LiBO_2$. The contents were then dissolved in dilute nitric acid (HNO_3) and analyzed by ICPES. Lead, Cd and As in the residues were determined using atomic absorption (AA) spectroscopy. The samples for these determinations were first digested with nitric and perchloric acids. The dissolved samples were then analyzed by flame atomic absorption spectrometry (Model 3030B, Perkin Elmer, Norwalk, CT). Arsenic was determined using a hydride generation system (Model MHS-1, Perkin Elmer) attached to a Model 603 atomic absorption spectrometer (Perkin Elmer). Oxide and chloride ratios for Zn, Fe, Pb, Cd, and As in smokepot residues were estimated by determining the water soluble and insoluble portions. The composition of the smokepot residue was then calculated by assuming that the water soluble fractions represent chlorides and the water insoluble fractions the oxides. Relative concentrations of major inorganic constituents in the homogenized pot residues from the two lots were then calculated.

RESULTS

Major Inorganic Constituents

A total of 39 smokepots were fired during the two trials. Thirty-five smokepots were from Lot # PB-84 M024-007 and four were from Lot # PB-84 C020-012. Smokepots were weighed before and after ignition; smokepot residues (2182 to 3297 g) were 16.0 - 24.4 percent of the original smokepot weight (e.g. Table 1). A record of burn rate, burn time, air temperature, and humidity was maintained in each trial. Burn times varied from 8:01 to 21:27 minutes (15:40 $\pm$ 3.05 average, 1 SD) for Lot # PB-84 M020-007 pots (Tables 1, 8) and 8:47 to 17:07 minutes (13:23 $\pm$ 3:41 average, 1 SD) for Lot # PB-84 C020-012 smokepots (Table 8). The difference between average burn times for the two lots was not statistically significant.

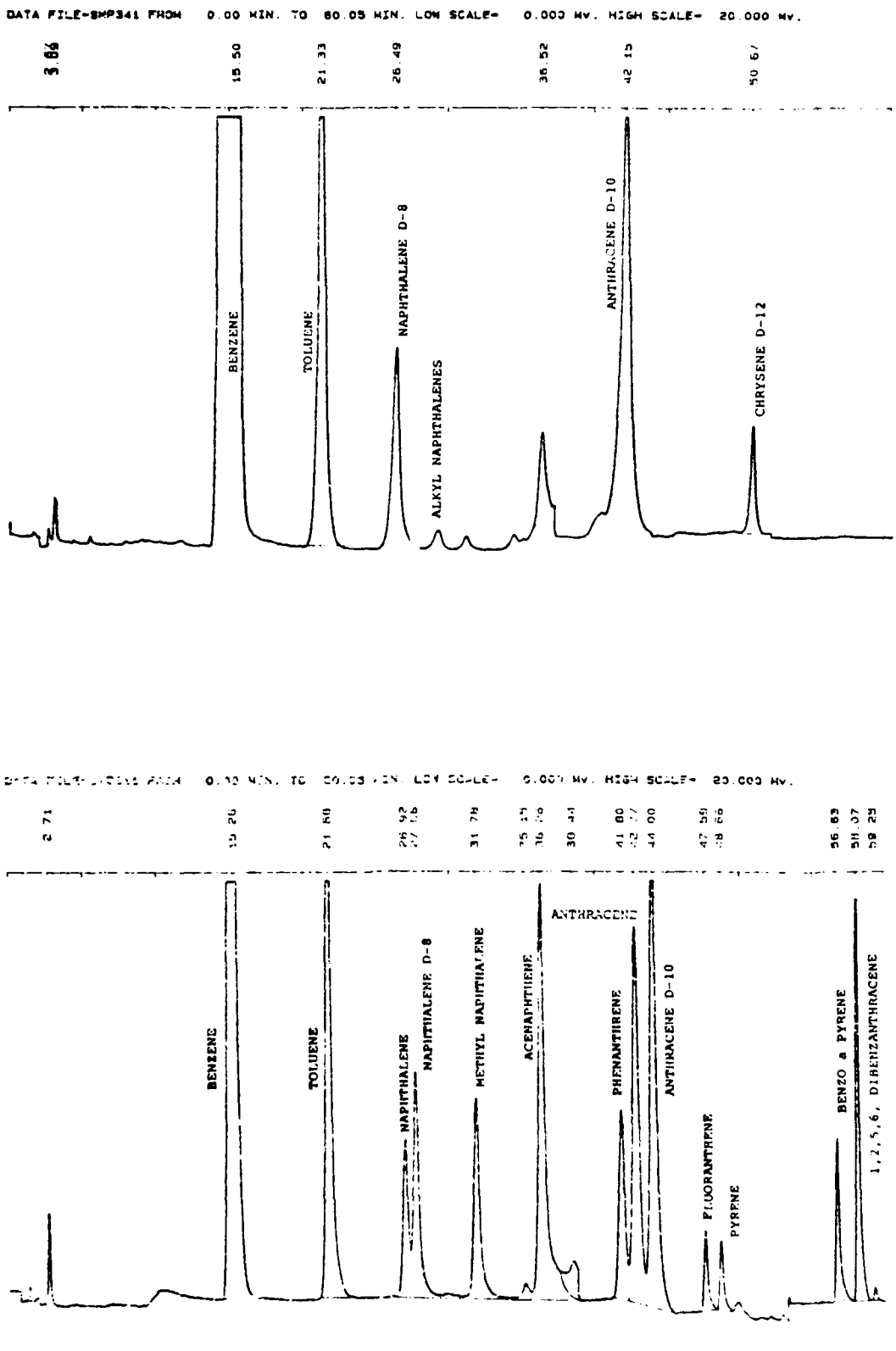


Figure 7. Chromatography of smokepot residue extract. Reverse phase HPLC with UV detector.
A. Sample B. Aromatic hydrocarbon stds.

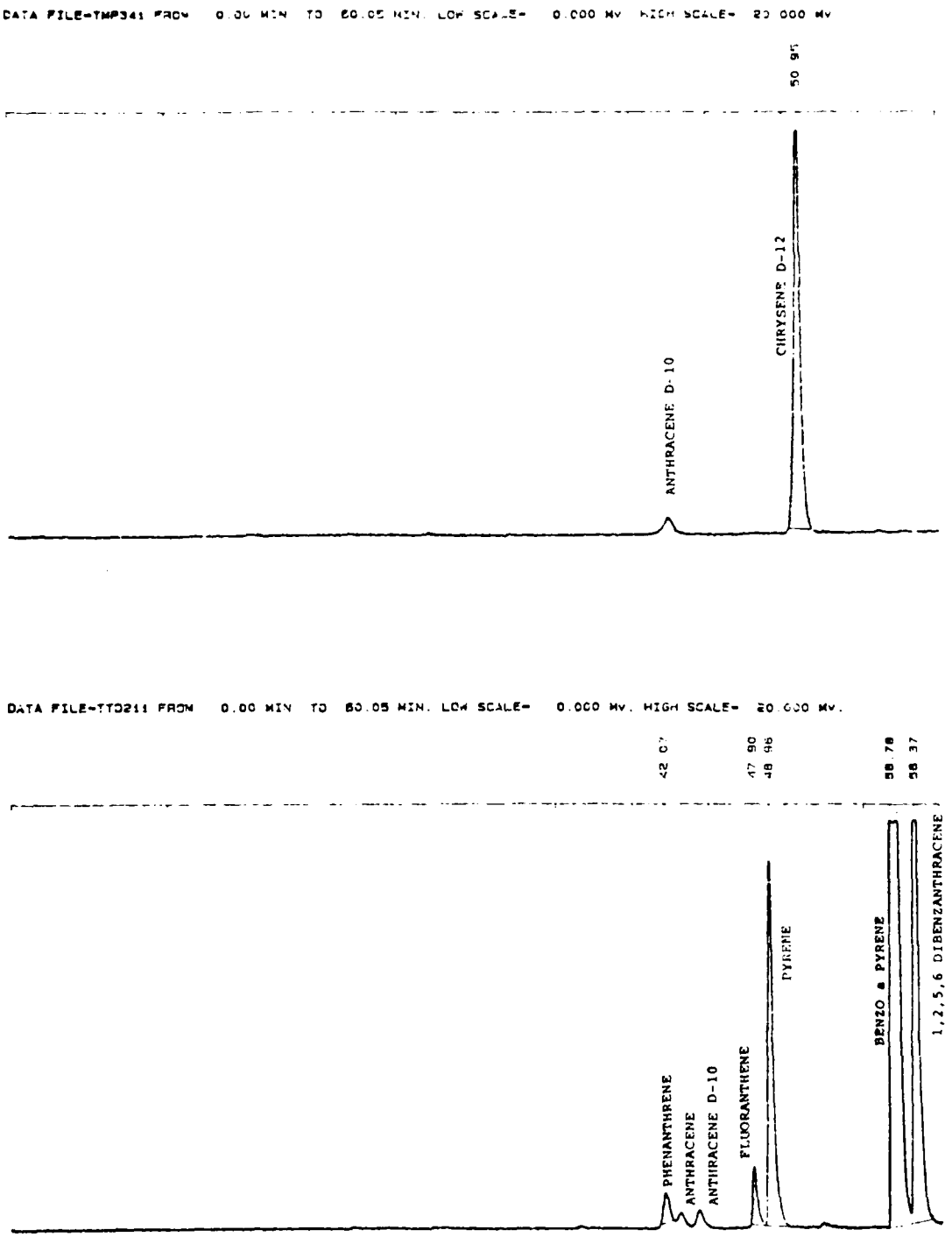


Figure 8. Chromatography of smokepot residue samples. HPLC with fluorescence detector.
A. Sample B. Aromatic hydrocarbons stds.

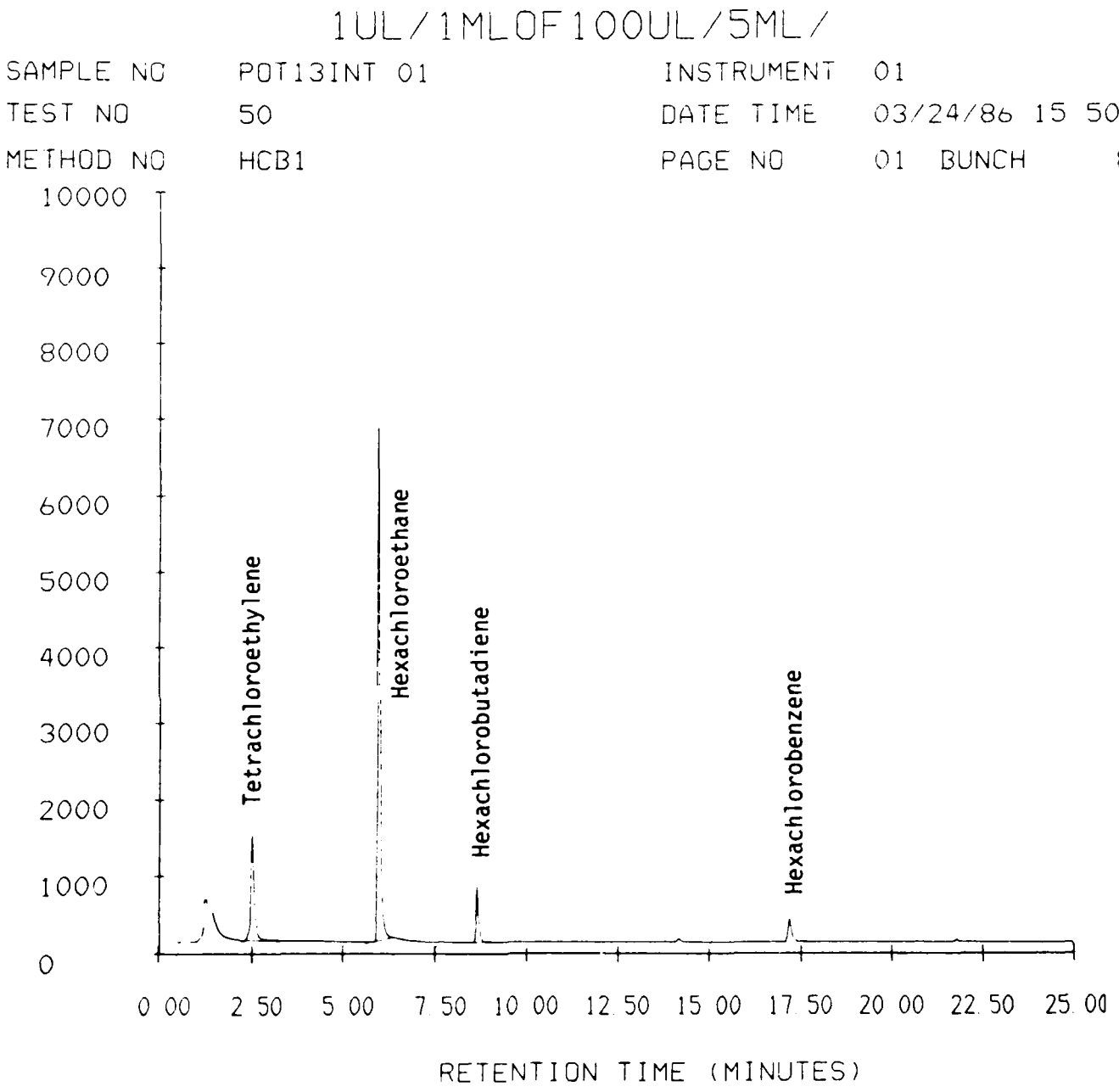


Figure 9. Chromatography of smokepot residue samples. Gas chromatograph with electron capture detector.

Smokepot residues were homogenized and analyzed for major inorganic and organic constituents according to the analytical scheme outlined earlier. The stoichiometric ratios of the smoke generation process (represented by equation 1) show that $ZnCl_2$, Al_2O_3 and carbon account for 76.3 %, 19.1 % and 4.5 % respectively of the total mass of the products. If substantial quantities of $ZnCl_2$ were lost as vapor/particulate matter from the smokepots, the major constituents of the residue in the smokepot would be Al_2O_3, elemental carbon, $ZnCl_2$, and residual ZnO. This was supported by the results obtained for residues from different burn modes.

Results for Trial 1 smokepots Trial 1 are given in Tables 2 and 3, and for smokepots from Trial 2 in Table 8. The major inorganic constituents were Al, elemental carbon, Zn and Fe. The predominant aluminum species was oxide, while Zn and Fe were present as chlorides and oxides. The discrepancies of 3.1 to 4.3 % in the material balance can be attributed to the error in analysis and to adsorption of moisture by the residue. The concentration of Al_2O_3 in smokepot residue was generally highest in the upper middle section A-1 (Table 3). This was expected, as this section contained the highest proportion of Al metal in the smokepot (to help the initial burn process). The carbon content increased towards the sides (section C). Appreciable quantities of chloride ion were also observed in this section. (It is possible than $ZnCl_2$ was trapped by the high carbon content of this section.)

Concentrations of Cd and As were generally below 1.0 ppm, although Cd concentrations in residues from Lot # PB-84 C020-012 reached 118 ppm. Concentrations of Pb, Cd and As in the residues differed between lots and were most likely related to the concentration of these elements in the smokepot munition. However, unlike the results reported by Katz et al. (1980), no direct correlation in the relative concentrations of Pb and Cd was found in the smokepot residue.

Major Organic Constituents:

Total extractable organics, primarily aromatic hydrocarbons and chlorinated aliphatics, were present at concentrations below 1 %. The chromatographic results obtained for representative smokepot residues are shown in Figures 7 - 9. Chromatograms from the four ignition modes did not differ. Recoveries for the model compounds (naphthalene to dibenzanthracene) were 85 % - 100 %. The predominant organic compounds found in Trial 1 smokepot residues were aromatic hydrocarbons (Table 5). Using the refined analytical method, chlorinated aliphatics were the major components of residues in the spent smokepots in Trial 2. Compounds were present at low levels only; most of the aromatic hydrocarbons i.e. naphthalene, methylnaphthalenes, dimethylnaphthalenes, trimethylnaphthalenes and methylphenols were at 0.2 - 2 ppm in

all residues. The predominant species are listed in Table 7, and shown in Figure 10.

Composite samples of smokepot residues from Trial 1 were analyzed for polychlorinated dibenzo-p-dioxins (USEPA 1984), a class of highly toxic compounds. These compounds have been shown to be formed during incineration of chlorinated organics such as polyvinylchloride and polychlorinated biphenyls, and others. The reaction conditions inside the incinerator, although occurring at a lower temperature, are somewhat similar to those in the smokepot. For these analyses, the three sections of residues at each depth for a given smokepot were combined; 15 samples were produced. All of these compounds were present at concentrations below 1.0 ppb. The low concentrations can be attributed to the very high temperatures [1100°C) (Van Voris et al. 1986) to > 1500°C (Katz et al. 1980)] reached during the smoke generation process, which lowers the chance of survival of most organics (Senkan 1982). Further, Senkan (1982) notes that the decomposition of chlorinated organics may be catalyzed by iron, zinc, and aluminum catalysts at relatively low temperatures. Carbon tetrachloride yields phosgene at temperatures as low as 100°C in the presence of iron, while chloroform, trichloroethylene, dichloroethane, and tetrachloroethylene (perchloroethylene, formed by pyrolysis hexachloroethane) give detectable amounts of phosgene around 300°C.

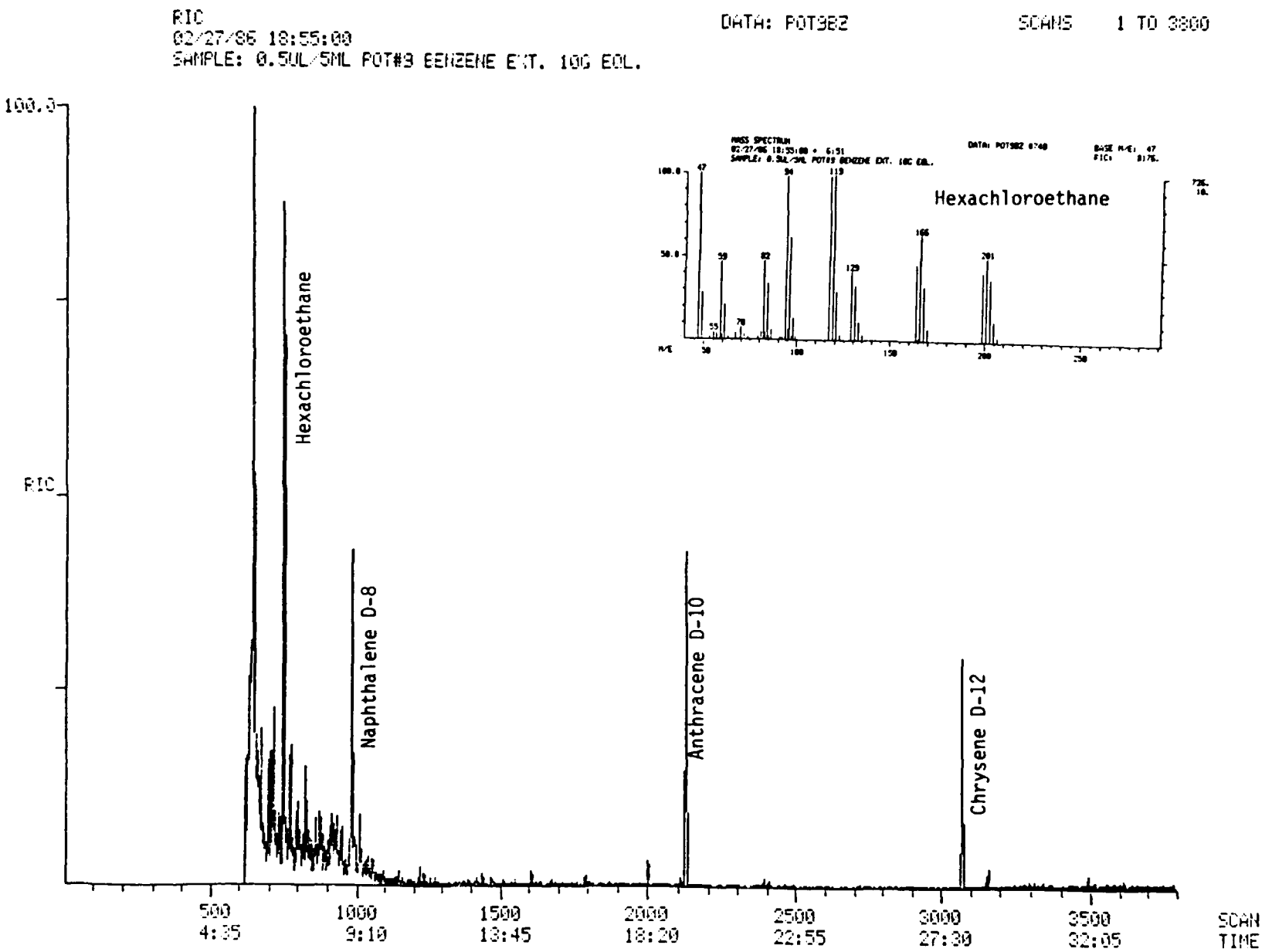


Figure 10. Total ion chromatogram of smokepot residue (collected in vicinity) extract.

Quantities of deposited residue varied with the burn mode (Table 13). The inorganic compositions of deposited and smokepot residues were usually about the same (Table 9). However, concentrations of organic compounds in residues from smokepots ignited on their sides were generally higher than in residues from upright smokepots (Table 11; Figures 11-12). Partially reacted materials were represented in these residues which contained as much as 15 % (by weight) hexachloroethane (HCE). The formation of hexachlorobutadiene (HCBUT) and hexachlorobenzene (HCB) were probably produced by dechlorination of HCE to perchloroethylene (PCE), dimerization of PCE to HCBUT, and addition of PCE to HCBUT followed by dechlorination (Eq. 2):

(Eq. 2)

$$C_2Cl_6 + Al + ZnO \longrightarrow ZnCl_2 + Al_2O_3 + C + heat$$

$$ZnCl_2 \xrightarrow{-Cl_2} C_2Cl_4 \text{ (PCE)} \longrightarrow C_4Cl_6 \text{ (HCBUT)} \xrightarrow{-Cl_2} HCB$$

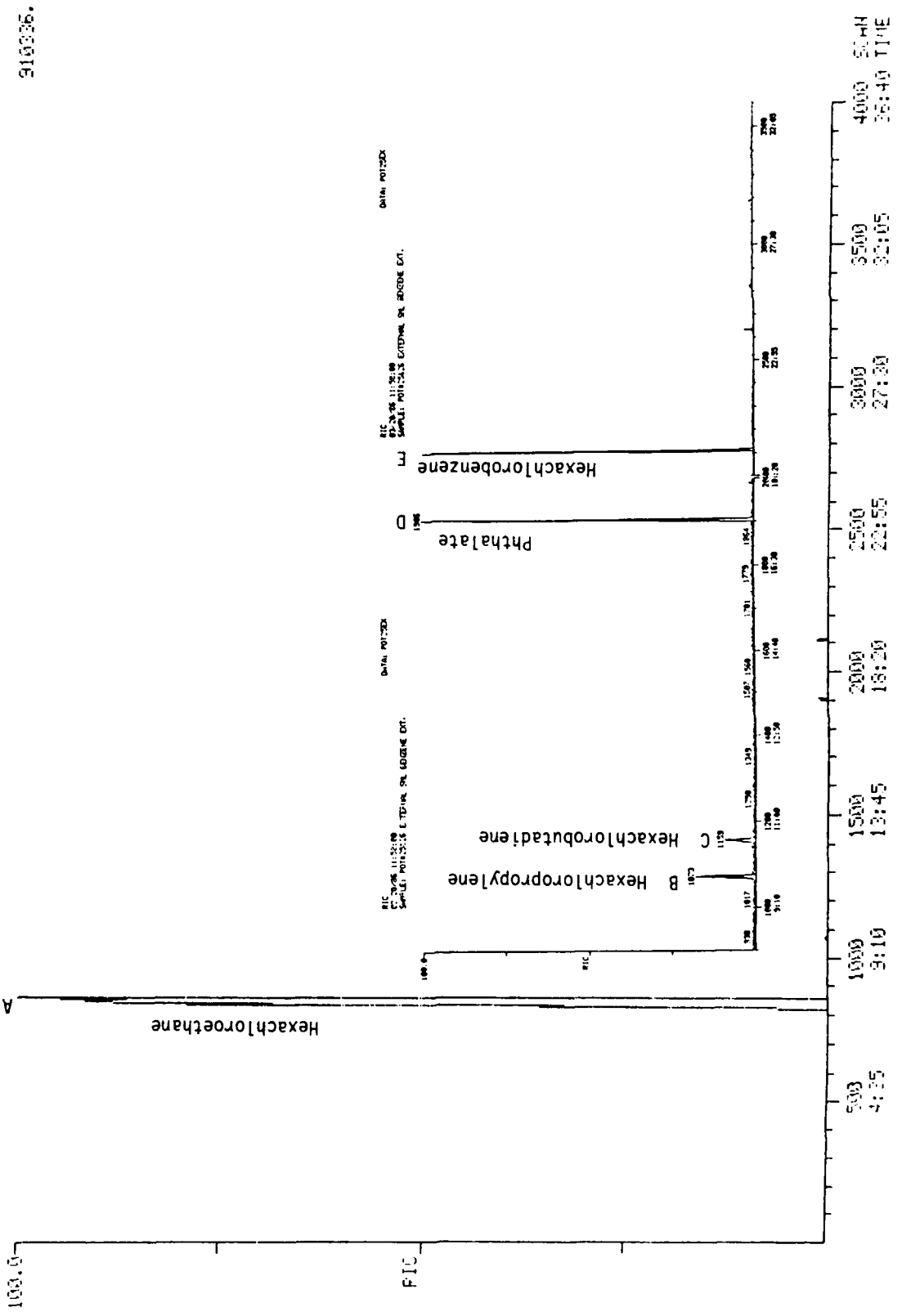


Figure 11: Total ion chromatogram of smokepot residue (collected in vicinity) extract.

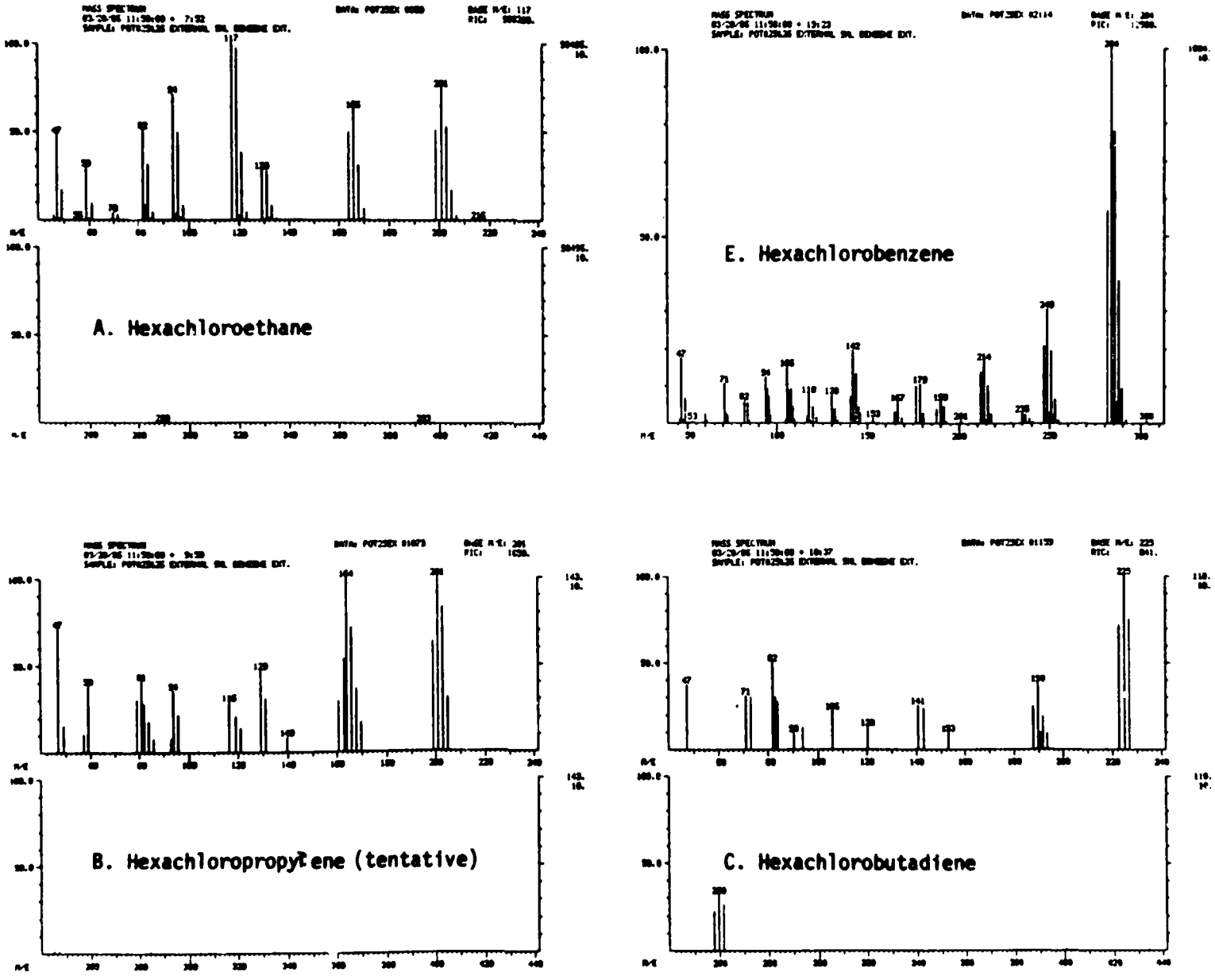


Figure 12. Mass spectra of major peaks shown in Figure 12

DISCUSSION

TRIAL 1: RANGE FINDING

Trial 1 was conducted at Ft. Leonard Wood, MO on June 24-25, 1985. Five smokepots from Lot # PB-84 M024-007 were ignited sequentially. Burn rate, burn time, ambient air temperature and humidity were monitored during each burn (Table 1). The air temperature was 37.5°C and the relative humidity was 54%. The purpose of this trial was to determine the homogeneity of organic and inorganic compound concentrations in residues remaining in the canister. The only combustion scenario considered was the upright single smokepot. In order to maximize the opportunities for data analysis, a balanced design with replication was used (Appendix A). Sampling bulk material is statistically complicated (Appendix A). We will refer to the set of smokepots used in a trial as a lot (not to be confused with Lot # of a given canister). Portions taken from the lot will be called samples (Venter 1982). In statistical terms, the smokepots constitute a "segmented" lot. A segmented lot is one that comes in partitioned form such as in packages, bales, cans or truckloads (Elder, Thompson and Myers 1980). Examples of nonsegmented lots are a tank of oil and a pile of coal.

Table 1: Burn Parameters for Trial 1 Smokepots, Lot # PB-84 M024-007

Pot #	Burn Weight (g) Initial	Final	Smokepot Residue, %	Burn Time (min:sec)
1	13,600	2922.6	21.4	16:57
2	13,600	2913.2	21.4	18:00
3	13,600	2900.8	21.1	16:17
4	13,800	3152.1	22.8	17:05
5	13,400	2373.8	17.7	15:47

The color and compactness of the residue varied with location in the canister. The middle section (Figure 3, section A) was whitish-gray in color, and the shade grew darker with depth, i.e. A-1 was the lightest and A-3 the darkest. Sections B and C were darker than A, suggesting a higher carbon content. The few orange areas at the top and along the side of the smokepot were probably $FeCl_3$. Material from each section was separately homogenized and analyzed for major inorganic and organic constituents according to the analytical scheme outlined earlier. The major inorganic constituents (Table 2) were Al, C, Zn and Fe. Aluminum was present mainly as oxide, while Zn and Fe were predominantly chlorides and, to a lesser extent oxides, in agreement with Eq. 1. Particularly to be noted are the concentrations of lead, which averaged 365 ppm (39 - 1280 ppm) and often exceeded 1000 ppm (0.1%). Average lead concentrations differed significantly across section (A=155, B=403, C=539 ppm), and decreased signifi-

cantly with depth (601, 349.5, 143.7 ppm); the section*depth interaction was not statistically significant (p = 0.222, 2-way analysis of variance).

Table 2: Residue Composition by Smokepot and Subsection
Trial 1, Lot # PB-84 M024-007

Pot	Section	INORGANIC CONSTITUENT Al	Zn	Fe	C	Pb	Cd	As
				%			(ppm)	
1	A 1	46.8	2.5	0.02	1	50	3.7	3.6
	A 2	43.7	2.1	1.1	1.2	75	0.72	2.0
	A 3	34.6	5.1	0.17	2.5	140	2.1	5.8
	B 1	47.4	0.85	0.3	5.6	39	0.34	3.0
	B 3	47.2	2.3	0.10	3.6	69	0.46	1.0
	C 1	37.0	2.3	0.02	29.6	420	4.2	2.0
	C 2	33.8	3.9	0.3	19.2	120	1.9	2.0
	C 3	42.4	2.7	2.1	7.6	140	0.52	3.8
2.	A 1	38.9	3.0	1.2		450	1.1	3.0
	A 2	47.2	1.7	0.32	1.2	120	0.38	6.0
	A 3	42.6	6.6	0.26	2.6	89	0.84	4.1
	B 1	37.0	7.2	3.2	12.1	1160	3.4	3.0
	B 2	42.5	4.5	1.2	5.6	750	1.7	2.0
	B 3	43.2	3.0	0.95	3.3	200	0.80	3.8
	C 1	27.0	15.0	1.2	38.1	980	11.0	3.4
	C 2	33.8	9.8	0.14	12.6	420	6.4	3.0
	C 3	40.8	1.6	0.08	5.3	68	0.69	7.2
3.	A 1	38.0	2.9	0.11	0.7	160	0.58	5.5
	A 2	44.5	2.7	0.08	0.1	55	0.31	0.8
	A 3	41.6	3.9	1.4	1.6	140	0.60	3.9
	B 1	38.2	2.4	1.4	5.1	370	0.39	4.1
	B 2	43.6	2.7	1.9	3.2	760	0.85	3.3
	B 3	41.9	2.3	0.2	3.3	75	0.33	3.5
	C 1	27.9	12.3	0.23	38.1	1010	9.0	4.5
	C 2	41.6	3.4	0.11	12.6	290	2.0	3.0
	C 3	41.8	4.5	0.06	5.3	100	0.70	3.5
4.	A 1	40.8	4.4	2.5	1.2	250	1.0	5.1
	A 2	43.5	5.8	0.74	1.0	190	0.93	3.7
	A 3	37.1	16.0	0.11	0.9	49	0.76	3.0
	B 1	44.0	4.0	2.4	5.1	510	1.0	3.2
	B 2	43.4	6.9	0.15	1.2	94	0.42	4.1
	B 3	38.6	12.4	0.03	4.3	47	0.49	3.3
	C 1	29.1	13.5	1.4	28.4	1030	6.5	3.6
	C 2	36.0	10.9	0.32	18.2	200	3.5	3.6
	C 3	36.3	12.1	0.06	6.8	87	1.2	4.0
5.	A 1	41.3	3.4	1.2		450	1.7	2.0
	A 2	44.0	2.1	0.09	2.6	59	0.24	3.0
	A 3	39.5	1.2	0.02	4.6	51	0.36	3.8
	B 1	37.1	5.2	2.6	12.0	940	0.41	1.
	B 2	39.2	3.3	1.5	8.5	480	0.21	2.0
	B 3	28.2	1.4	1.5	3.9	160	0.55	2.0
	C 1	28.8	12.0	2.2	29.3	1200	8.3	1.0
	C 2	33.6	9.4	3.1	22.6	1280	7.8	<0.8
	C 3	36.6	5.0	1.3	10.8	740	3.1	3.0

Based on the stoichiometric ratios represented by equation 1, $ZnCl_2$ accounts for 76.5%, Al_2O_3 19.1%, carbon 4.5%, of the total mass of the products. If most of the $ZnCl_2$ was lost as vapor/particulate matter from the smokepots, the major compounds in the smokepot residue would be Al_2O_3 and C. This is generally supported by Table 2. Other inorganic constituents detected in the residue were Fe and Pb, with concentrations between 1% and 50 ppm respectively. Arsenic and cadmium concentrations were 0.2 to 6.0 ppm. Concentrations of Pb, Cd and As in the residues were most likely related to their concentrations in the smokepot munitions, although a direct correlation was not shown. Ionizable chloride concentrationss (determined by ion chromatography) were highest in section C of the smokepot residue (Table 3). The predominant species was probably $ZnCl_2$. Ferric chloride ($FeCl_3$) was formed to a lesser extent by reaction of HCl formed during the smoke generation with the smokepot casing.

Table 3: CONCENTRATION OF IONIZABLE CHLORIDES

Pot #	Section	Concentration (% of solid residue)
2	A*	
	B*	7.5
	C*	11.2
3	A*	4.2
	B*	4.2
	C*	8.4
4	A*	4.
	B*	4.6
	C*	12.0
5	A*	5.0
	B*	6.0
	C*	12.0
6	A 2	4.2
	A 3	
	B 1	5.8
	B 2	5.0
	B 3	4.2
	C 1	16.0
	C 2	12.0
	C 3	6.0

*Composite sample incorporated subsections 1, 2, and 3.

The homogeneity of the distributions of metals and carbon in the smokepot were evaluated by statistical analysis. A nested analysis of variance (ANOVA) design was used in which depths were nested within sections and smokepots were replicates. The

results are summarized in Table 4. The concentration of Al_2O_3 was generally highest in the upper middle section, A-1, reflecting the high aluminum metal concentrations used in this section of the smokepot to help the burn process. However, differences in the concentrations of total aluminum in the residue were not statistically significant. The analytical concentration of carbon varied significantly ($p > 0.95$) across sections and depths. Concentrations were highest at the sides and at the top (i.e. C-1), where they reached 38%. Appreciable quantities of zinc and chloride ion were found, especially in the outer section (C) of the smokepot. The chemical analyses suggested that $ZnCl_2$ was probably trapped by the high carbon content of this section. However, concentrations of Zn (all species), As and Fe within a smokepot did not differ statistically. Lead concentrations were significantly different across sections but not depths and Cd concentrations differed both across sections and depths.

Table 4: Results of Nested Analysis of Variance - Trial 1

	MEAN SQUARES			F RATIO	
ELEMENT	DEPTH	SECTION	ERROR	DEPTH*	SECTION**
Aluminum	5301.4	3782.7	4323.6	1.40	0.88
Zinc	67.1	21.3	13.7	3.15	1.56
Iron	1.4	1.1	0.8	1.34	1.34
Carbon	1188.1	286.1	9.1	4.05#	31.46#
Lead	567758.9	343554.2	80921.3	1.65	4.25#
Cadmium	59.3	17.5	2.4	3.38#	7.26#
Arsenic	2.8	1.99	1.87	1.41	1.06

*2,35 degrees of freedom (critical value = 3.27; p = 0.95)
F = Depth mean square/Section mean square
**6,35 degrees of freedom (critical value = 2.29; p = 0.95)
F = Section mean square/Replication mean square
#Equals or exceeds appropriate critical value.

Aromatic hydrocarbons were the major organic compounds found in spent smokepot residues (Table 5). Most concentrations (i.e. naphthalene, methylnaphthalenes, dimethylnaphthalenes, trimethylnaphthalenes and methylphenols) were 2-10 ppm in all canister sections. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans concentrations in composite samples were below the detection limit of 1 ppb. Chlorinated aliphatics were not found. The probable mechanism of loss was through $AlCl_3$-catalyzed Friedel-Crafts alkylation of the toluene (Morrison and Boyd 1966, p. 385) used as the extractant.

Table 5: Major Organic Compounds Found in Trial 1 Smokepot Residues

Pot	Section	Major Organic Constituents
1, 3	A	Traces (< 1 ppm) of naphthalene, methylphenol, mono-, di-, trimethyl naphthalenes
	C	Naphthalene (~1 ppm); other constituents similar to section A
3	C	Naphthalene (~1 ppm); methylphenol 92 ppm; all others similar to section A (< 1 ppm)

The organic compounds in deposited residues differed from those found in the smokepot residues. Most of the deposited material was collected within 1 meter of the smokepot; little or no material was found in collection plates set at distances greater than 2 meters from the smokepot. The mass of deposited residue collected at distances from the smokepot are given in Table 6. Defining lwt = log (weight + 1) and ldist = log (distance + 1), the relationship between weight and distance was consistent with exponential dieoff (Eq. 3):

$$lwt = 2.367 - 1.383\ ldist \qquad (r^2 = 0.908,\ 13\ df) \qquad \text{(Eq. 3)}$$

To assess the ecological importance of deposited residues, estimates of the quantity of material deposited at each distance are needed. The corrected weight (cwt in g/m^2) was obtained from Table 6 by dividing the raw weight (g) by the proportion of the area sampled. The mean corrected weights were 237 g/m^2 (0.5 m), 507 g/m^2 (2 m), 46.7 g/m^2 (5 m). Defining lcwt = log (corrected weight + 1), regression gave the relationship (Eq. 4):

$$lcwt = -8.010\ ldist^2 + 14.870\ ldist \qquad (r^2 = 0.993,\ 13\ df) \qquad \text{(Eq. 4)}$$

An estimate of the maximum distance residue was distributed, 5.4 m, was obtained by setting lcwt to zero in Eq. 4. An estimate of the total mass of material deposited within 5.4 m from a single upright smokepot, 2945 g, was obtained by numerically integrating Eq. 4 between the limits 0 m and 5.4 m. The deposited material was about 30% of the mass deposited during ignition, or about 22% of the initial smokepot mass.

Table 6: Mass of Residue Collected Downwind of Smokepots, Trial 1

Pot #	Distance (M)	Weight (g)	% Area Sampled
1	0.5	6.62	2.56
1	2.0	1.02	0.17
1	5.0	0.07	0.03
2	0.5	5.00	2.56
2	2.0	0.48	0.17
2	5.0	0.00	0.03
3	0.5	3.76	2.56
3	2.0	0.65	0.17
3	5.0	0.00	0.03
4	0.5	6.69	2.56
4	2.0	0.58	0.17
4	5.0	0.00	0.03
5	0.5	8.28	2.56
5	2.0	1.58	0.17
5	5.0	0.00	0.03

Chemical characterization of deposited compounds was limited by small amounts of sample and contamination of samples during storage and extraction with toluene. The major organic compounds in the residue were hexachloroethane (100-500 ppm), hexachlorobenzene (5-150 ppm), hexachlorobutadiene (5 ppm) and phenols. A summary of the analyses is given in Table 7. Many other compounds, mainly aliphatic hydrocarbons, were also found. These compounds probably reflect contamination during storage of the samples in polyethylene bags and glass vials with polyethylene liners.

Table 7: Organic Constituents of Residues Collected 0.5 m Downwind of Smokepots - Composited Samples, Trial 1

Pot #	Constituents	Concentration ppm	Concentration g/m^2
1	Hexachloroethane	220.0	0.057
	Hexachlorobenzene	20.0	0.0052
	Hexachlorobutadiene	12.0	0.0031
	Methylnaphthalenes	10.0	0.0026
	Chlorinated phenol	5.0	0.0013
2	Hexachloroethane	120.0	0.023
	Hexachlorobenzene	15.0	0.0029
	Methylnaphthalenes	2.0	0.0004
3	Hexachloroethane	500.0	0.073
	Hexachlorobenzene	50.0	0.0073
	Hexachlorobutadiene	15.0	0.0022
	Methylphenols	50.0	0.0073
5	Hexachloroethane	220.0	0.071
	Hexachlorobenzene	50.0	0.016
	Methylphenols	200.0	0.065

Conclusions from Trial 1

Characterization of the smokepots showed that 17-23% of the original mass remained in the smokepot as residue, primarily as inorganic oxides and chlorides (Al_2O_3, carbon, $ZnCl_2$, $FeCl_3$, Fe_2O_3). Trace amounts of Pb, Cd and As were also found. Organic constituents were a minor portion of total residue mass. The identified organic compounds were aromatics such as naphthalene, alkylnaphthalenes and methylphenols. The material collected outside the smokepot contained many chlorinated organics such as tetrachloroethylene (TCE), hexachloroethane (HCE), hexachlorobenzene (HCB), hexachlorobutadiene (HCBUT), and chlorophenols. The deposited residues were characterized by unused and partially used reactants and their products.

TRIAL 2: CHARACTERIZATION OF RESIDUES FROM FOUR BURN CONFIGURATIONS

In Trial 2, 34 smokepots were ignited using four burn modes: (1) single smokepot upright, (2) double smokepot upright, (3) single smokepot on side, (4) double smokepot on side. Concentrations of major inorganic and organic species found in the smokepot residues and distributed outside ignited smokepots are given in Tables 8 and 9, respectively.

Tables 8 and 9 suggest that Lot # PB-84 C020-012 residues differed from Lot # PB-84 M024-007 residues. Differences in the composition of smokepot residues in Table 8 are examined in Table 10. One-way analysis of variance showed that for both a single smokepot and a stack of two smokepots ignited horizontally, Al, Zn, Cd and As levels in the smokepot residue differed between lots. Aluminum levels were higher in residues from Lot # PB-84 M024-007, while Zn, Cd, and As levels were higher in residues from Lot # PB-84 C020-012. Similarly, although the data (Table 9) are very limited, the composition of residues deposited from Lot # PB-84 C020-012 and Lot # PB-84 M024-007 differed. For mode 2 (double upright smokepots), concentrations of Zn, C, Pb, Cd, HCE, HCBUT, and HCB were higher, and Al and TCE lower, in Lot # PB-84 C020-012. For burn mode 4 (double smokepots on side), Pb, Cd, TCE, HCE, HCBUT, and HCB concentrations were higher, and Al was lower, in Lot # PB-84 C020-012. Because of lot-related differences, only the 30 smokepots from Lot # PB-84 M024-007 were considered in most of the later analyses.

Table 8: Inorganic and Organic Species found in Smokepot Residues: Trial 2

	Concentration (%)					Concentration (ppm)							Burn Time
Pot	Al	Fe	Zn	C	EXT	Pb	Cd	As	TCE	HCE	HCBUT	HCB*	(Min:Sec)
Mode 1, Single Smokepot Upright Air Temperature 3°C, Relative Humidity 65%													
01	39.6	0.25	1.10	3.65	0.60	14.0	0.60	1.0	32.30	19.80	1.300	0.070	17:16
02	40.7	0.47	5.06	2.94	0.60	74.0	0.90	0.9	12.50	9.80	0.820	0.090	17:07
03	35.7	0.24	1.61	2.91	.	67.0	0.60	0.8	10.20	4.00	0.680	0.050	17:14
04	42.9	0.30	5.60	3.04	0.70	110.0	0.90	0.8	9.80	6.50	1.020	0.040	18:20
Mean	39.7	0.32	3.34	3.14	0.63	66.3	0.75	0.9	16.20	10.03	0.955	0.062	
Mode 2, Double Smokepot Upright Air Temperature 1°C, Relative Humidity 65%													
05	40.4	1.20	4.10	9.68	2.15	220.0	1.90	0.8	13.60	7.80	0.050	0.050	12:14
06	41.4	0.32	2.93	5.37	1.12	38.0	0.70	0.8	7.20	4.80	0.080	0.050	16:06
07	45.7	0.91	2.90	6.56	0.60	140.0	1.00	0.8	10.80	6.70	0.200	0.080	15:34
08	42.9	0.27	2.13	2.64	0.39	69.0	0.60	0.8	10.40	4.00	0.230	0.120	18:47
09*	26.2	0.72	22.80	3.70	0.22	340.0	118.00	3.6	6.15	5.00	1.020	0.330	15:27
10*	29.2	0.46	24.40	1.96	0.24	46.0	79.00	3.0	.	.	.	.	17:07
11	40.2	0.71	1.24	5.08	0.52	130.0	0.90	0.8	10.25	3.75	0.720	0.025	17:53
12	40.6	0.19	3.45	3.76	0.62	32.0	0.60	0.9	10.05	2.05	0.675	0.016	17:57
13	43.9	0.66	2.06	6.70	0.86	100.0	1.80	0.8	26.00	4.75	1.150	0.150	14:04
14	38.1	0.17	5.16	3.50	0.34	43.0	0.60	0.8	7.75	4.00	0.670	0.330	16:33
15	43.8	0.34	2.62	5.10	.	77.0	1.00	0.8	.	.	.	.	16:32
16	42.0	0.14	4.55	3.43	.	15.0	0.60	0.8	6.25	0.90	0.048	0.080	18:13
Mean	41.9	0.49	3.11	5.18	0.83	86.4	0.97	0.8	11.37	4.31	0.425	0.100	
Mode 3, Single Smokepot on Side Air Temperature -13°C, Relative Humidity 65%													
17	35.4	0.32	3.19	3.46	0.81	110.0	0.60	0.8	8.50	0.72	0.040	0.030	15:54
18	40.4	0.36	2.15	3.69	0.66	72.0	0.60	0.8	14.00	2.50	0.320	0.350	21:27
19	35.1	0.23	7.60	1.47	0.61	52.0	0.60	0.8	14.00	0.28	0.470	0.046	17:10
20	40.4	0.34	1.97	3.35	0.59	140.0	0.60	0.8	10.00	1.45	0.490	0.070	15:13
21	32.2	0.12	2.06	3.28	0.73	78.0	0.60	0.9	19.00	5.75	0.290	0.040	18:11
22	44.1	0.18	6.19	2.12	0.37	94.0	0.60	0.8	33.00	5.00	0.850	0.030	17:02
Mean	37.9	0.26	3.86	2.90	0.63	91.0	0.60	0.8	16.42	2.62	0.410	0.094	

Table 8: continued

Pot	Concentration (%) Al	Fe	Zn	C	EXT	Concentration (ppm) Pb	Cd	As	TCE	HCE	HCBUT	HCB$	Burn Time (Min:Sec)
Mode 4, Double Smokepot on Side Air Temperature -10°C, Relative Humidity 54%													
23	41.1	0.97	3.15	3.28	0.93	160.0	2.10	0.8	5.25	0.21	0.425	0.030	9:21
24	42.9	0.21	2.45	2.04	0.75	41.0	0.60	0.8	.	.	.	.	15:36
25$	28.1	1.17	24.80	3.72	0.36	190.0	74.00	2.9	6.25	0.47	.	.	8:47
26$	29.0	0.38	24.10	4.35	0.23	260.0	63.00	3.5	16.00	1.80	1.450	0.060	12:12
27	41.3	0.96	4.04	9.80	1.46	260.0	2.00	0.8	11.00	2.70	0.670	0.020	11:43
28	38.9	0.59	2.42	8.20	1.62	170.0	2.00	0.8	0.31	0.23	0.120	0.030	17:12
29	39.5	0.30	1.73	3.60	0.74	43.0	0.60	0.8	0.05	0.05	0.040	0.010	12:23
30	43.0	0.18	4.61	1.17	0.55	25.0	0.60	0.8	12.50	1.50	1.100	0.005	16:25
31	44.2	0.53	2.86	1.31	0.90	180.0	0.60	0.8	.	.	.	.	8:35
32	43.2	0.40	2.65	2.12	0.33	56.0	0.60	0.8	15.00	2.05	0.080	0.020	11:24
33	41.6	0.74	2.76	4.11	1.29	110.0	1.00	0.8	18.00	2.10	1.470	0.010	8:01
34	38.4	0.33	1.35	2.27	0.97	76.0	0.60	0.8	17.00	1.45	2.000	0.010	12:51
Mean	41.4	0.52	2.80	3.79	0.95	112.1	1.07	0.8	9.89	1.29	0.738	0.017	
F$$	2.9	1.51	0.56	1.78	0.95	0.6	0.64	0.5	1.17	7.78$	1.61	1.69	

*EXT=extractable organics
TCE=tetrachloroethylene, HCE=hexachloroethane,
HCBUT=hexachlorobutadiene, HCB=hexachlorobenzene
# Lot # PB-84 C020-012; unmarked smokepots are Lot # PB-84 M024-007
$ Significant ($p \geq 0.95$)
**F-test

Table 9: Inorganic and Organic Species Deposited from Ignited Smokepots: Trial 2

		Concentration (%)					Concentration (ppm)						
Pot	Mass*	Al	Fe	Zn	C	EXT	Pb	Cd	As	TCE	HCE	HCBUT	HCB**
Mode 1, Single Smokepot Upright													
01	7.3	45.6	0.22	9.0	0.89	0.39	31	0.6	0.8	1000	1960	6.2	15.4
02	17.4	40.1	0.62	11.7	0.48	0.52	59	0.9	0.8	1100	2060		21
03	20.5	34.6	0.48	16.8		3.86	49	5.3	0.8	16800	1300	48.5	21
04	38.2	42.2	0.38	8.9	0.12	0.93	72	3.5	0.8	75000	2194	8.6	13.4
Mode 2, Double Smokepot Upright													
5+6	37.9	37	0.49	13.9		1.93	72	3.5	0.8	60000	5800	16.3	8.53
7+8	21.3	35.6	0.81	15.5		1.06	160	3.7	0.8	30000	3100		25.6
9+10#	26.9	30	1.14	17.8	1.68	1.41	230	92	0.8	10614	7200	36.4	37
11+12	25.0	39.3	0.84	10.3	0.92	0.81	120	2.6	0.8	1018	1040		5.9
13+14	33.0	36.6	0.66	13.9	0.61	1.61	170	2.3	0.8	27260	10570	1.3	2.98
15+16	24.2	37.8	0.51	13.4	0.1	0.75	130	1	0.8	27200	10570	1.3	2.98
Mode 3, Single Smokepot on Side													
18	14.7	29.7	1.4	21.1	1.94	2.08	55	69	0.8	1636	18440	9.4	328.5
19	54.1	28.6	0.58	17.5	3.28	7.21	75	15	0.8	40000	56200	143.1	298.5
20	55.3	37.5	0.36	14.6	0.68	4.32	24	1	0.8	15700	39900	8.6	20.9
21	26.5	22	0.63	18.8	2.04	9.2	73	25	0.8	1226	15200	576.9	111.9
22	44.7	22	0.63	18.8	2.04	9.2	73	25	0.8	10480	144000	837.6	582.1
Mode 4, Double Smokepot on Side													
23+24	45.7	23.7	0.55	20.4	3.72	9.9	61	16	0.8	42260	105000	98.3	402
25+26#	286	20.8	0.56	20.6	4.3		190	240	1	53000	79300	358.9	1477
27+28	84.9	32.4	0.66	13.7	9.9	1.5	120	26	0.8	7600	3740	68	238
30-34	***Samples could not be collected because of snow on ground****												

*Mass = total residue mass (g) collected between 0.5-2 m.
**TCE=tetrachloroethylene, HCE=hexachloroethane,
HCBUT=hexachlorobutadiene, HCB=hexachlorobenzene
#Lot # PB-84 C020-012; unmarked smokepots are Lot # PB-84 M024-007

Table 10: One-way Analysis of Variance Comparing Smokepot Residues from Lots # PB-84 C020-012 and # PB-84 M024-007

Mode 2 Double Smokepot Upright

	Al	Fe	Zn	C	EXT	Pb	Cd	As	TCE	HCE	HCBUT	HCB
N OF CASES#	10	10	10	10	8	10	10	10	9	9	9	9
MINIMUM	38.100	0.140	1.240	2.640	0.340	15.000	0.600	0.800	6.250	0.900	0.048	0.016
MAXIMUM	45.700	1.200	5.160	9.680	2.150	220.000	1.900	0.900	26.000	7.800	1.150	0.330
MEAN	41.900	0.491	3.114	5.182	0.825	86.400	0.970	0.810	11.367	4.306	0.425	0.100
STANDARD DEV	2.226	0.361	1.213	2.078	0.592	62.789	0.492	0.032	5.916	2.109	0.391	0.096
N OF CASES##	2	2	2	2	2	2	2	2	1	1	1	1
MINIMUM	26.200	0.460	22.800	1.960	0.220	46.000	79.000	3.000	6.150	5.000	1.020	0.330
MAXIMUM	29.200	0.720	24.400	3.700	0.240	340.000	118.000	3.600	6.150	5.000	1.020	0.330
MEAN	27.700	0.590	23.600	2.830	0.230	193.000	98.500	3.300	6.150	5.000	1.020	0.330
STANDARD DEV	2.121	0.184	1.131	1.230	0.014	207.889	27.577	0.424	0.000	0.000	0.000	0.000

Compound	Bartlett	F***	Prob	Mean	SD	Pooled SD	T	Prob
Al	0.004	0.004	0.957	39.53	5.92	2.22	8.28	0
Fe	0.580	0.435	0.515	0.51	0.33	0.35	0.37	0.72
Zn	0.008	0.006	0.938	6.53	8.06	1.21	21.94	0
C	0.377	0.281	0.600	4.79	2.12	2.01	1.51	0.16
EXT	6.401	5.765	0.024	0.71	0.58	0.55	1.36	0.21
Pb	4.518	3.820	0.061	104.17	94.21	88.71	1.55	0.15
Cd	49.466	-95.263	1.000	17.23	38.87	8.73	14.42	0
As	24.199	55.315	0	1.23	0.98	0.14	23.38	0
HCBUT****							2.85	
TCE****							-13.26	
HCE****							1.43	
HCB****							2.23	

Table 10: continued

Mode 4 Double Smokepot on Side

	Al	Fe	Zn	C	EXT	Pb	Cd	As	TCE	HCE	HCBUT	HCB
N OF CASES*	10	10	10	10	10	10	10	10	8	8	8	8
MINIMUM	38.400	0.180	1.350	1.170	0.330	25.000	0.600	0.800	0.050	0.050	0.040	0.005
MAXIMUM	44.200	0.970	4.610	9.800	1.620	260.000	2.100	0.800	18.000	2.700	2.000	0.030
MEAN	41.410	0.521	2.802	3.790	0.954	112.100	1.070	0.800	9.889	1.286	0.738	0.017
STANDARD DEV	1.969	0.291	0.971	2.928	0.402	77.462	0.677	0.000	7.177	1.008	0.724	0.010
N OF CASES*	2	2	2	2	2	2	2	2	2	2	1	1
MINIMUM	28.100	0.380	24.100	3.720	0.230	190.000	63.000	2.900	6.250	0.470	1.450	0.060
MAXIMUM	29.000	1.170	24.800	4.350	0.360	260.000	74.000	3.500	16.000	1.800	1.450	0.060
MEAN	28.550	0.775	24.450	4.035	0.295	225.000	68.500	3.200	11.125	1.135	1.450	0.060
STANDARD DEV	0.636	0.559	0.495	0.445	0.092	49.497	7.778	0.424	6.894	0.940	0.000	0.000

Compound	Bartlett	F***	Prob	Mean	SD	Pooled SD	T	Prob
Al	1.321	1.01	0.323	39.27	5.32	1.88	8.84	0
Fe	1.079	0.82	0.373	0.56	0.33	0.33	1.00	0.340
Zn	0.578	0.43	0.516	6.41	8.47	0.93	29.92	0
C	2.738	2.19	0.151	3.83	2.65	2.78	0.11	0.912
EXT	1.956	1.53	0.227	0.84	0.45	0.38	2.22	0.050
Pb	0.286	0.21	0.648	130.92	75.14	75.14	1.94	0.081
Cd	21.587	40.25	0	12.31	26.36	2.54	34.24	0
As	24.199	55.32	0	1.19	0.95	0.14	22.63	0
TCE	0.003	0.00	0.964	10.14	6.75	7.14	0.22	0.83
HCE	0.008	0.01	0.938	1.26	0.95	1.00	0.19	0.85
HCBUT****							2.37	
HCB****							1.22	

* Lot # PB-84 M024-007
** Lot # PB-84 C020-012
*** 1,26 degrees of freedom
**** Computed using the standard deviation from Lot # PB-84 M024-007.

With the exceptions of Al and HCE, mean concentrations of inorganic and organic compounds in Lot # PB-84 M024-007 smokepot residues were independent of the burn mode. The similarity of pot residue compositions from the four burn modes contrasts with deposited residue compositions.

Concentrations of Al, Zn, C, extractable organics, Pb, HCE, and HCB in Lot # PB-84 M024-007 deposited residues were related to burn mode (Table 11). Aluminum concentrations decreased smoothly from Mode 1 to Mode 4 and Zn, C, EXT, HCE and HCB concentrations increased. Lead concentrations in residues from vertically ignited smokepots were lower than in residues from horizontally ignited smokepots; residues from single and double smokepots for an orientation had about the same Pb concentration. Organic compounds were at least an order of magnitude higher in residues deposited from smokepots ignited on their sides than in residues deposited from smokepots ignited upright. Levels of organics were comparable for single and double smokepots for a given burn orientation. These results show that changes in the burn scenario appreciably affected the dispersion of compounds in the environment. For example, a horizontal smokepot contributed the larger mass of a given compound/gram deposited residue although the upright smokepot deposited more total mass.

Table 11: Means for Deposited Residues Trial 2 Lot # PB-84 M024-007

Burn Mode	Average Concentration						
	Al %	Zn %	C %	EXT %	Pb ppm	HCE ppm	HCB ppm
1 (1 pot, up)	40.6	11.6	0.5	1.4	53	1878	17.7
2 (2 pot, up)	36	14.1	0.68	1.3	147	6380	13.8
3 (1 pot, side)	28	18.2	2	6.4	60	54748	217
4 (2 pot, side)	25	18	5.9	5.7	124	62680	673

Concentrations of compounds in smokepot and deposited residues were usually uncorrelated. Exceptions (mode) were positive correlations for Al (2), Zn (2), C (2,4), Pb (1), Cd (2). If mode is not considered, concentrations of Al, Zn, Pb, Cd, HCE in pot and deposited residues were positively correlated.

To further explore the effects of burn mode, separate discriminant functions were developed for the smokepot residues and deposited residues from Lot # PB-84 M024-007. The discriminant function was developed using only those compounds differing between modes (Al, Zn, C, extractable organics, Pb, HCE, HCB) for the deposited residue. Also, for the deposited residue, mode averages replaced missing C values for smokepots 3, 5+6, 7+8.

A k-means non-hierarchical [illegible] (three) discriminant coordinates developed for each [illegible] explained by Romesburg (1984, p. [illegible]): "With [illegible] k objects are initially used as [illegible] objects are tentatively assigned to [illegible] nearest in distance ('most similar to'). What [illegible] of the k-means methods apart is how the initial [illegible] selected to be seeds, and how the process [illegible] initial set of k seeds to the final set [illegible] rounding them." Our use of the [illegible] agreement with findings noted above. The [illegible] formed a single cluster. In contrast, the deposited [illegible] samples generally clustered by burn mode (table [illegible]) which supports the conclusion that the burn mode affected the [illegible] tion of the deposit. (Clusters developed using deposited [illegible] raw data were meaningless.) The table first gives the [illegible] statistics from an analysis of variance performed for each of the discriminant factors. The statistically significant F ratios indicate that each of the three discriminant factors differs among burn modes; clusters formed from nonsignificant discriminants are meaningless. Next, the members of each cluster are given. The first cluster is formed by upright smokepots from burn mode 1 and some double upright pots from mode 2. The second cluster comprises the mode 3 single horizontal smokepots. Cluster 3 is formed by the double horizontal pots, and cluster 4 is formed by double upright smokepots.

TABLE 12: SUMMARY STATISTICS FOR K-MEANS CLUSTERING ON DISCRIMINANT COORDINATES*

VARIABLE	BETWEEN SS	DF	WITHIN SS	DF	F-RATIO	PROB
FACTOR(1)	94.454	3	12.131	12	31.143	.000
FACTOR(2)	-51.105	3	10.631	12	-19.229	1.000
FACTOR(3)	7.774	3	11.662	12	2.666	.095

CLUSTER NUMBER: 1

MEMBERS			STATISTICS				
POT	MODE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST. DEV.
1	1	1.30	FACTOR(1)	-10594.77	-10593.72	-10592.86	.81
2	1	.27	FACTOR(2)	-8037.36	-8035.67	-8034.14	1.17
4	1	.78	FACTOR(3)	-525.94	-525.10	-523.84	.71
5+ 6	2	.90					
11+12	2	1.02					

CLUSTER NUMBER: 2

MEMBERS			STATISTICS				
POT	MODE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST. DEV.
3	1	1.13	FACTOR(1)	-10591.69	-10589.83	-10588.36	1.15
18	3	.60	FACTOR(2)	-8036.13	-8035.44	-8034.76	.46
19	3	.95	FACTOR(3)	-527.62	-526.55	-525.30	.91
20	3	.81					
21	3	.54					
22	3	1.12					

CLUSTER NUMBER: 3

MEMBERS			STATISTICS				
POT	MODE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST. DEV.
23+24	4	1.07	FACTOR(1)	-10585.85	-10585.19	-10584.52	.66
27+28	4	1.07	FACTOR(2)	-8034.21	-8033.21	-8032.21	1.00
			FACTOR(3)	-526.27	-524.85	-523.43	1.42

CLUSTER NUMBER: 4

MEMBERS			STATISTICS				
POT	MODE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST. DEV.
7+ 8	2	.15	FACTOR(1)	-10594.68	-10594.61	-10594.52	.07
13+14	2	.29	FACTOR(2)	-8032.71	-8032.13	-8031.67	.43
15+16	2	.34	FACTOR(3)	-526.32	-526.11	-525.89	.18

* Mode average used for C concentrations for Smokepots 3, 5+6, 7+8.

Deposition profiles (Table 13) showed that the quantity of deposited material increased in going from a single smokepot to double pots, and in going from a vertical to horizontal position during ignition. This is most easily seen by comparing the rows labeled "mean" (or the "Summary") and by examination of Figure 13 which the means at each distance for each mode are plotted against distance. Horizontally placed smokepots deposited about twice as much material as the same number of smokepots placed upright at distances out to 2 m (Table 13, Summary). Two upright smokepots contributed about 40% more mass than a single upright smokepot. Two horizontal pots contributed 80-100% more mass than a single horizontal smokepot.

Quadratic relationships through the origin (like Eq. 4) were developed for each burn mode. Area correction factors for modes 1-2 (3-4) were 0.12 @ 0.5 m, 0.04 (0.58) @ 1 m, 0.04 (32) @ 1.5 m 0.03 (0.20) @ 2 m. The inflection point of the quadratic curve was used to estimate the distance at which the mass of deposited material peaked. This point was about 1.7 m for all modes. The non-zero root of the equations was used to estimate the distance at which the collected mass fell to zero. The estimates were 7.0 m and 6.2 m for modes 1 and 2, and 6.0 m and 5.6 m for modes 3 and 4. These points are shown in Figure 13 as a, b and c, d, respectively. These results were unanticipated; the a priori expectations were that the peak and dieoff distances for the horizontally placed smokepots would be farther than for upright smokepots. The data suggest that horizontal smokepots have the sharper deposition gradient. The fairly uniform deposition gradient from upright pots causes tailing, so dieoff occurs more gradually.

From the quadratic relationships developed, it is estimated (by integration) that a single upright smokepot deposited 871 g and double upright smokepots deposited 1228 g of material within 7 m. Estimates for a single and double horizontal smokepot were 110 g and 196 g. These results suggest that doubling the number of pots increased the quantity of material deposited within 7 m by 40 to 80 percent. Upright smokepots deposited 8 times the quantity of material deposited from a similar configuration of horizontal pots. The reasons for this are not known. Perhaps when the smokepot is in the horizontal position material which would have settled out was either vaporized by the intense heat of the flame (which shot out at least 0.5 m) or resuspended by its force. The results suggest that if resuspension occurred, horizontal smokepots might be more efficient at producing obscuration because less material is deposited near the smokepot and the direction of the deposited material can be controlled. We speculate that the heat of the flame and resuspension would result in different particle size distributions for the two burn orientations.

Table 13: Deposition Profile of Smokepot Residues

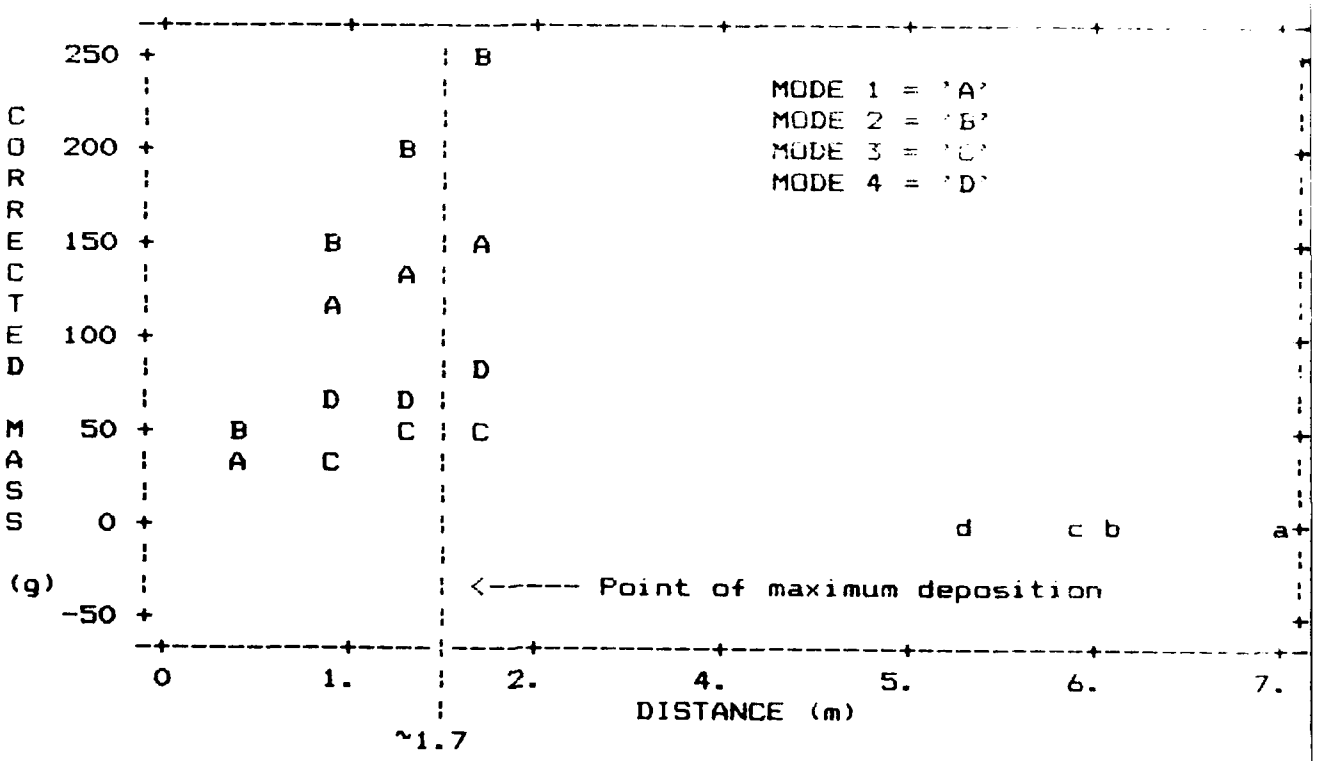
Pot #	Collection Amounts (g)				Total (g)
Collection Dist.	0.5	1.0	1.5	2.0	
Mode 1 (Upright single smokepot)					
1	0.3	1.6	2.1	3.1	7.3
2	3.0	6.3	3.7	4.3	17.4
3	3.4	5.4	4.2	3.1	20.5
4	8.7	12.7	9.8	6.9	38.2
mean*	3.9	6.5	5.0	4.4	20.9
Mode 2 (Upright double smokepot)					
5-6	3.9	9.0	12.2	12.8	37.9
7-8	3.9	6.2	5.4	5.6	21.3
9-10**	4.5	7.6	7.3	7.5	26.9
11-12	4.3	8.7	6.6	5.4	25.0
13-14	5.8	10.7	8.2	8.3	33.0
15-16	5.1	7.6	6.3	5.2	24.2
mean	4.6	8.4	7.7	7.5	28.3
Mode 3 (Single smokepot on side)					
18	**	6.0	4.9	3.8	14.7
19	**	28.7	17.1	8.3	54.1
20	**	25.4	19.0	10.8	55.3
21	**	14.9	7.6	3.8	26.5
22	**	19.9	9.2	15.6	44.7
mean	**	18.9	11.6	8.5	37.1
Mode 4 (Double smokepot on side)					
23-24	**	23.3	13.3	9.1	45.7
25-26***	**	82.6	123.5	79.5	285.7
27-28	**	43.2	23.8	17.9	84.9
29-34	Samples could not be collected because of snow.				
mean	**	33.3	18.6	13.5	65.3

*For Lot # PB-84 M024-007
**Sample not collected because this distance was in combustion zone.
***Lot # PB-84 C020-012

Summary:

Mode	Mean*				
1	3.9	6.5	5.0	4.4	20.9
2	4.6	8.4	7.7	7.5	28.3
3	.	18.9	11.6	8.5	37.1
4	.	33.3	18.6	13.5	65.3

Figure 13: Average Mass versus Maximum Dispersion Distance



Conclusions from Trial 2

The statistical results for Trial 2 suggested that the composition of smokepot and deposited residues were related to Lot #. For a given Lot #, the smokepot residue composition was not affected by the burn mode, although the composition of the deposited residue (Table 11) depended on both the burn configuration (single or double smokepot) and the orientation (upright or horizontal placement). As expected, about twice as much material was deposited by a stack (either upright or horizontal) of two smokepots than by a single smokepot. Hrizontal smokepots were expected to deposit more material than upright smokepots, but the reverse was found. However, a smokepot lying on its side deposited 5-10 times more organics than an upright smokepot and, except for Al, higher levels of metals. Table 11 shows that doubling the number of smokepots for a given burn mode generally did not double the concentration of a given compound. The major exception was HCE deposited from upright smokepots.

Relationships between deposited concentrations without regard to burn mode are given as Spearman rank correlation coefficients in Table 14. Aluminum, zinc, carbon, extractable organics, and HCE were highly correlated. Deposited concentrations of Zn, C, extractable organics, HCE and hexachlorobenzene decreased as the concentration of deposited Al increased. In contrast, deposited concentrations of Zn, C, HCE, hexachlorobenzene, and extractable organics, were positively correlated. The concentration of deposited lead was correlated, inversely and weakly, only with deposited hexachlorobenzene.

TABLE 14: MATRIX OF SPEARMAN CORRELATION COEFFICIENTS FOR EMITTED RESIDUES, TRIAL 2, N = 13

Constituent	Al	Zn	C	EXT	Pb	HCE
Al	1.000					
Zn	-0.895	1.000				
C	-0.708	0.592	1.000			
EXT	-0.906	0.846	0.636	1.000		
Pb	-0.174	-0.110	0.019	-0.025	1.000	
HCE	-0.824	0.851	0.457	0.879	-0.099	1.000
HCB	-0.708	0.725	0.766	0.675	-0.359	0.680

ENVIRONMENTAL SIGNIFICANCE

This study has shown that a single upright M[illegible] smokepot deposits several hundred grams to more than a kilogram of residue within 5-7 m downwind and laterally around the smokepot. Under good weather conditions (i.e. low wind velocity) a single upright smokepot could deposit 3 kg, as found in Trial 1. Assume that 1 kg is deposited in a semi-circular area of radius 7 m and that the residue is in the first 0.5 cm of the soil. The volume of contaminated soil is 196,350 cm^3 [that is, $3.14(700)^2(0.5)/2$]. Assuming a bulk density of 1.58 g/cm^3 for the A horizon of soil in tracked areas (Diersing and Severinghaus 1984), the average concentration of residue in the soil would be 3227 mg/kg [i.e. 10^6 mg/(196,350 cm^3 x 1.58 g cm^{-3})]. If the deposition area was 7 m, the concentration in the soil would be 1644 mg/kg [i.e. 3227 $(5/7)^2$ mg/kg]. From Table 9, the average lead concentration in deposited residue from a single upright pot was (21+59+49+72)/4 = 52.75 ug Pb/g residue. Hence, a single upright pot would deposit 170.0 ug Pb/kg soil [52.75 ug Pb/g residue (3.223 g residue/kg soil)]. Estimated soil loads (ug contaminant/kg soil) from a single upright pot for the other compounds in Table 9 are: Al=1,310,000; Fe=137,000; Zn=371,500; C=16,000; EXT=45,900; Cd=8.3; As=2.6; TCE=19,665 (based on geometric mean); HCE=6054; HCBUT=68.0; HCB=57.0.

Aluminum, zinc, and chlorinated hydrocarbons are present in the deposited residue at levels exceeding 1000 mg/kg residue. Assuming that most of the deposition is within 5 m of the smokepot, as above, the soil concentrations of these compounds contributed by the residue from a single smokepot could exceed 3 ug/kg. The lower levels (500 mg/kg residue) of cadmium, arsenic, lead, and iron in the deposited residue would increase soil concentrations by 1 ug/kg. For comparison, Illinois regulations for the application of sewage sludge to agricultural land limit the incremental amount of Cd which is added to 2 lbs/acre/yr to a maximum of 10 lbs. In establishing this limitation to protect soils and crops from Cd poisoning, the State assumed that normal plowing would incorporate the sludge into the first foot of soil. Using these figures, and assuming a soil density of [illegible] cm^3, the annual limitation is about 600 ug/kg soil.

Both HC smoke and individual constituents in the combustion mix, the residue, and smoke, are of toxicological concern. Rabbits and rats, for example, exposed to single doses of hexachloroethane-zinc oxide smoke and observed for up to 14 days exhibited changes in the respiratory tract. These changes included acute inflammation and in some cases necrosis of the laryngeal and tracheal mucosa. Pulmonary edema and pneumonitis were observed in decedent animals. Animal that survived to the end of the experiment showed similar but much less severe changes in the respiratory tract (Marrs et al. 1981). [illegible] Cichowicz (1983), most of the major [illegible]

obstacle mixture or its residues, such as Al, Cd, HCE, and others, are of toxicological concern. Aluminum, for example, is implicated in Alzheimer's disease. Roberts (1982) states that elevated levels of aluminum have been implicated in senile dementias of the Alzheimer's type (SDAT) and cautions (p. 175) that "extra sources of entry of this metal should be eliminated insofar as is possible."

According to the classification system of Cassarett and Doull (1975), hexachloroethane is moderately to very toxic to mammals; the lowest published lethal dose (LDLo) for intravenous administration to dogs is 325 mg/kg and to rabbits by subcutaneous administration, 4000 mg/kg. It can be absorbed from the gastrointestinal tract, through the lungs, and through the skin. Industrial experience shows that an excessive amount of HCE dust in the air can cause irritation to the skin and mucous membranes. According to Cichowicz (1983, p 32): "The dust has been assigned a moderate hazard rating that may involve both irreversible and reversible changes, but not severe enough to cause death or permanent injury." Hexachloroethane is a reported animal carcinogen (IARC 1979; Gold et al. 1984), with a relative carcinogenic potency estimated from the linearized multihit model, S, of 0.014 mg/kg-day. Gold et al. (1984) report a standardized carcinogenic potency of 319-359 mg for hexachloroethane, expressed as the tumorigenic dose rate for 50% of the test animals for a given target site(s) (TD50). Hexachloroethane is regulated by USEPA as a drinking water contaminant.

Cadmium, another constituent of HC smoke and HC smokepot residues, is a suspect human carcinogen (IARC 1976). As reported by USEPA, the relative potency of cadmium of 6.65 mg/kg-day makes it more carcinogenic than chlordane (S = 1.61 mg/kg-day), beryllium (S = 2.6 mg/kg-day), chloroform (0.07 mg/kg-day), nickel (1.15 mg/kg-day), and vinyl chloride (0.0175 mg/kg-day), among other well known carcinogens. Reif (1984) reported that although singly, neither smoking nor exposure to cadmium appeared to be a carcinogen for renal cancer, the group exposed to both had an increased risk of 450%. Glaser et al. (1986) have reported the results of a thirty-day inhalation study of cadmium compounds by male Wistar rats continuously exposed to submicron aerosols of 0.1 mg/m^3 Cd as $CdCl_2$ or CdO; the total inhaled Cd was 0.55 mg. Most of the cadmium was found in the lung cytosolic compartment. The mean white blood cell counts were elevated at the end of the inhalation period; mean serum activity of the alanine aminotransferase (GPT) was significantly elevated for the cadmium oxide exposed rats. Other effects were also observed. We expect that the effects observed in rats will follow the normal inter-species scaling relationships, and estimate that humans will exhibit signs of Cd toxicity at 0.55 mg $(0.2 \text{ kg}/70 \text{ kg})^{0.25}$ = 0.13 mg. From the data in Glaser et al. (1986) and Novak et al. (1984), the estimated quantity of Cd inhaled by a soldier exposed to HC smoke under the Fort Irwin scenario (Novak et al. 1984; exposure to 1 pot at 50 m) as 0.47 mg. Additional exposure to Cd will

occur from deposited materials and canister residues during cleanup, thereby increasing the likelihood that physiologically active levels of cadmium will be taken in.

On ingestion or contact, zinc chloride, the prime aerosol constituent of HC smoke, affects the lungs, skin, eyes, liver, and other organs. The general toxicology of zinc chloride has been reviewed (Cichowicz 1983). The inhalation toxicology of zinc oxide, an HC smokepot reactant and emitted by product, has been reported recently by Lam et al. (1985). They studied functional and morphologic changes in the lungs of guinea pigs exposed by nose only for 3 hr/day for 6 days to freshly formed zinc oxide particles (projected area diameter = 0.05 um, σ_g = 2.0) at 5 mg/m^3, the currently recommended threshold limit value (TLV). Vital capacity, functional residual capacity, alveolar volume, and diffusing capacity for carbon monoxide (DL_{CO}) were all decreased following the last exposure and did not return to normal values by 72 hr. Increases in flow resistance and decreases in compliance and total lung capacity returned to normal by 72 hr. Lung weights were elevated due to inflammation involving the proximal portion of the alveolar ducts and adjacent alveoli; these changes were still present at 72 hr. Lam et al. (1985) conclude from these results that "the current TLV for ZnO may not be adequate."

The Toxic Substances Control Act (TSCA) of 1976 addresses the manufacture, importation, distribution, and use of chemical substances. Cichowicz (1983) found that present HC smoke mix materials were inventoried on the initial TSCA Inventory list. Some HC smoke constituents are listed under RCRA (40 CFR 261.33). Hexachloroethane is a listed hazardous waste constituent, item U131, and disposal of residues containing hexachloroethane is regulated by RCRA although use of hexachloroethane during training is not regulated. Phosgene is a by-product of HC smoke and is listed as acutely hazardous, Item P095. Carbon tetrachloride, a by-product of HC smoke generation, is listed as a hazardous waste constituent, Item U127. Hexachlorobenzene is also a by-product and is listed as a hazardous waste constituent, Item U127. "Items listed as hazardous waste are not considered a hazardous waste until they are finally identified for disposal in accordance with DARCOM Supplement No. 1 to AR200-1 [32 CFR 650]" (Cichowicz 1983). However, wastes are defined by RCRA as "hazardous" if specifically listed by regulation or if exhibiting any one of the characteristics of reactivity, corrosivity, ignitability, or EP toxicity (as defined in 40 CFR 261.2).

An EP toxicity test was run on a sample of smokepot residues. Concentrations of lead (0.71 $\pm$ 0.05 mg/l) and cadmium (0.088 $\pm$ 0.002 mg/l) in the leachate were below the applicable standards of 5 mg/l and 1 mg/l, respectively.

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Appendix [illegible] Statistical Aspects of [illegible]

Following Elder et al. (1980), we are interested in estimating the mean and variance of a lot stored in N segments (i.e., smokepots). The procedure requires randomly selecting rn of N segments and partitioning them into r subsets (i.e., composites) of n segments each. We take p samples per segment, so each composite consists of np samples. We randomly select s of the S possible subsamples from each composite (S an integer) and run t tests on each subsample. For example, consider an initial trial using N = 6 smokepots. We can partition them into r = 3 subsets of n = 2 segments each. From each segment, p = 4 samples are taken, so the composite is formed by thoroughly mixing the np = 2 x 4 = 8 samples. If the mass of a composite relative to the mass required for analysis is large, then s = 1 ≤ S subsamples can be taken from each composite, otherwise only s = S = 1 subsamples can be taken. On each subsample we perform t tests. For our purposes, all the analyses performed on a (sub)sample is a test; i.e., we take t = 1.

The mathematical solutions of the expressions for the mean and variance are complicated, as are the resulting equations. An additional complicating factor in the analysis of the smokepots is the need to separately sample and analyze the top, middle and bottom levels of the smokepot residues. This situation can be handled within the framework of the model by forming composites at each level and allowing the variance due to levels to be part of the variance due to composites. Unfortunately, explicit answers to some of the questions that arise in choosing a sampling procedure cannot be given because some of variance components are themselves functions of n which vary differently in different applications. Because of high testing costs, the number of tests on each lot, rst, is usually small. The most common choice is rst = 1. If we can afford to run two tests per lot, we must decide whether to take r, s, or t equal to two. Given rst = 2, we can check for changes in the basic parameters using either two composites (r = 2 and s = t = 1) or two subsamples (r = t = 1 and s = 2).

Reporting Data

Because we are interested in comparing variability across pots, sites within a smokepot, and levels within a site, a logical reporting format is a matrix of the following type:

	Concentration																
Smokepot	I									II						....	
Site	1			2			3			1			2			3	....
Level	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a b c	
Compound																	
Anthracene																	
.	.																
.	.																
.	.																
Zinc chloride																	

A similar matrix would be used for the deposition samples.

Statistical Analysis

The statistical design for the analysis of the smokepot residue data is a nested factorial design.

If a two level design is used, the levels are:

Level	Factor	Maximum index
2	smokepots	6
1	sites within smokepot	4 (3 sites + pseudo site for composite)
0	levels	4 (3 levels + composite)

In order to get replication, composites have a pseudo site index of 4 and a pseudo level index of 4. For example:

```
1 1 1 200                (first smokepot, upwind, value = 200)
1 4 4 250, 300, 395      (first smokepot, composites)
```

If a three level design is used, the levels are:

Level	Factor	Maximum index
3	smokepots	6
2	sites within smokepot	3
1	composite	3
0	levels within composite	4 (3 levels + composite)

END

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